Studies on functional cellulose sheets prepared by dual polymer systems

$$\left(\begin{array}{c}\text{二成分高分子系により調製される}\\\text{機能性セルロースシートに関する研究}\end{array}\right)$$

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Chapter 1

General Introduction

1.1 Cellulose

Cellulose is one of the biosynthesized polysaccharides consisting of glucoses photosynthesized in plants from carbon dioxide and water, and defined as a linear homo-polysaccharide which is formed by β-1,4 glycoside bond of anhydro-D-glucoses (Figure 1.1). Cellulose is stored in plants such as wood, cotton, and seaweed so that they make it mainly to support their living bodies as a main component. Figure 1.2 shows the hierarchical structure of wood cellulose. Cellulose molecules produced in plants constitute the crystalline structure defined as cellulose I, where cellulose chains are aligned parallel to each other and packed side by side to form microfibrils with width of nanometer scale during biosynthesis. About the biosynthesis and crystalline structure of cellulose microfibril, numerous studies have been reported. [1-5] In plant, cellulose microfibrils form bundles with widths of > 15 nm. [6] Cellulose fibers with widths of 20-30 µm and lengths of 1-3 mm consist of the microfibril-bundles, and the fibers consist in tracheids or vessels with hemicellulose and lignin. [7] Wood tissue is composed mixture of cellulose, hemicellulose and lignin.
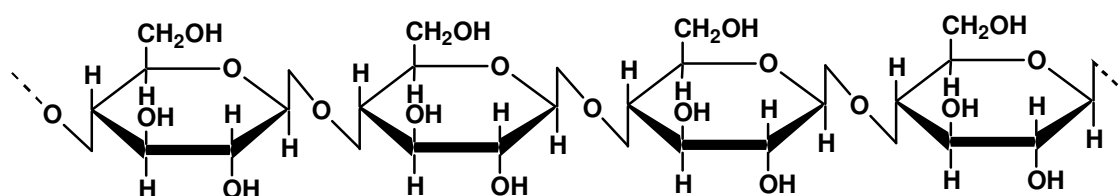
Figure 1.1 Chemical structure of cellulose formed by β-1,4 glycoside bond of anhydro-D-glucoses.

The amount of annual production of cellulose may be more than 100 billion tons, which are almost equal to the combined annual production of commodity type petroleum-based polymers such as poly(ethylene), poly(propylene), poly(ethylene terephthalate), poly(styrene), and poly(urethane). [8, 9] Therefore, cellulose is not only the most abundantly produced organic polymer material on any earth, but also reproducible and biodegradable biomass material, that does not pollute any environments even by disposing it, different from petroleum-based polymers. Cellulosic

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materials have been applied in various stages of our daily lives such as wood materials for building products and household furniture, paper materials for writing/printing and wrapping, woven or nonwoven materials for clothes, towels, wipes, napkins and diapers, coating materials for medical products, film materials for liquid crystal panels, powder materials for foods and cosmetics [10], [11].
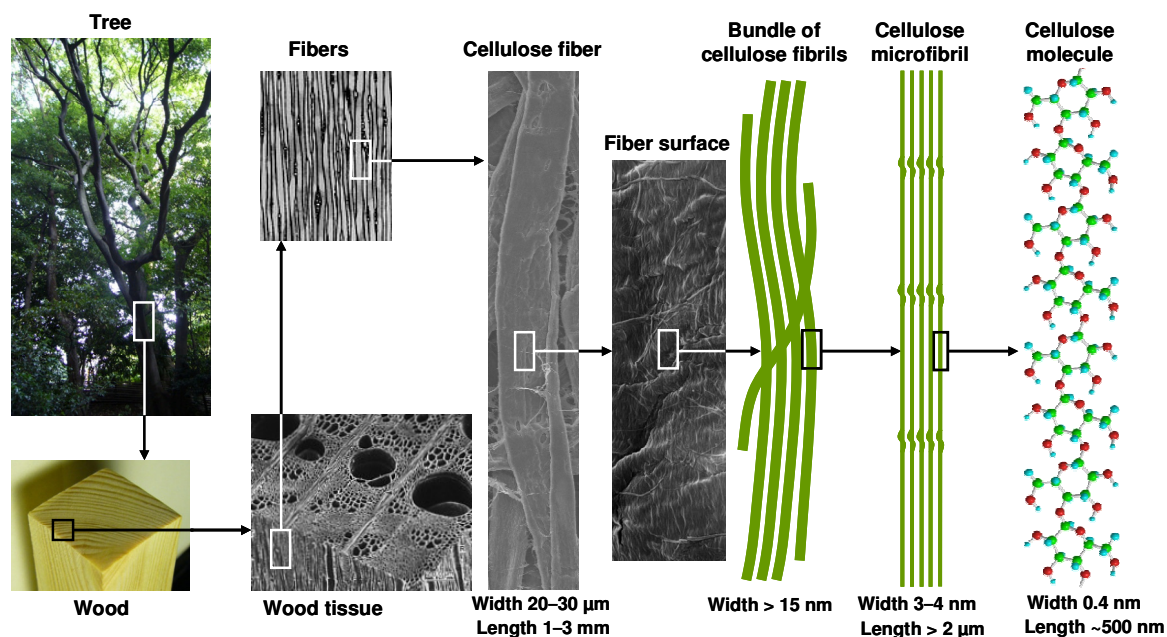
Figure 1.2 Hierarchical structure of wood biomass consisted of cellulose.

In the future, it will become more important to promote the applications of cellulosic materials for various industries more than now, in order to solve the problems of shortage of fossil resources and of environmental damages on earth due to usages of petroleum-based materials.

1.2 Applications of Cellulose to Paper Sheet Items

As mentioned in section 1.1, cellulosic materials have been applied to various items. Especially, cellulose fibers extracted from plants have been consumed as paper sheet materials, which are formed by inter-fiber hydrogen bonds (Hydrogen bonds). The basic paper-making method was established in China 2100 years ago, and paper sheet materials have been used as the media to record something, the communication tools, or wrapping materials for a long time. [11] In modern paper sheet-making industry, various types of paper sheet products have been developed: printing paper (coated paper and newspaper), wrapping paper, paper container, paper board, sanitary paper (diaper and

napkin) and household paper (paper towel and tissue) etc. (Figure 1.3). Such products
have been widely used in various stages of our lives.

Newspaper (Printing paper)	Coated printing paper (Printing paper)	Wrapping paper (Printing paper)
Paper container	Cardboard box (Board paper)	Diaper (Sanitary paper)
Paper towel (Household paper)	Tissue (Household paper)	Tissue (Toilet paper) (Household paper)

Figure 1.3 Photos of paper sheet products.

Though cellulose fibers used in traditional paper sheet were extracted from non-wood
biomass such as ramie, hemp, and some grasses by classical pulping processes, the
cellulose fibers prepared by chemical cooking of wood chips (Kraft process or Sulfite
process) are consumed in modern paper industry. [7), 10), 11)]

1.3 Functional and Innovative Paper Sheet Materials

Paper sheet products depicted in section 1.2 are commodities, and their basic

performances seem to be saturated except for sanitary sheet products in these days. Therefore, functional and innovative paper sheet materials for other applications different from commodities are required in industry field.

Cellulose fiber or inorganic fiber/functional inorganic particle composites are representative examples of functional sheet materials for the next generation [12-19]. Functional inorganic particles have been applied in various industries as catalysts, adsorbents, and ion-exchangers, [20, 21] although, such particles have powder forms and are hard to be handled in industrial process or laboratory scale. Moreover, some functional inorganic particles are expensive, and have some problems about the ways to tailor the functional materials in which the particles could show the best performance. From this point of view, composites of fiber and functional particle are expected to exert synergistic effects because particles can be retained in sheets consisting of fibers in high yields, and the retained particles have large surface areas.

Ichiura *et al.* succeeded in incorporating efficiently zeolite powders into an inorganic paper matrix by adopting a dual polymer papermaking system with cationic and anionic polymers as retention agents of zeolite. [12, 13] The absorption behavior of acetaldehyde, one of the typical volatile organic compounds (VOCs) to the zeolite-containing sheets was investigated in detail. [14]

As another example, heat- and steam-generating sheet materials are produced by papermaking technique using a dual polymer system. The heat- and steam-generating mats, which consist of iron powder, activated carbon powder, vermiculite, water-absorbing polymer like sodium polyacrylate, and a NaCl solution, have been produced by some manufacturing companies. These mats have a positive effect on enhancement of blood circulation, and are effective in stiff shoulders, eyestrain, and so on when attached to human bodies. [22, 23] However, some iron particles in the mats are not oxidized, because all iron particles are packed and blended heterogeneously in the "thick" mats and all particle components and oxygen are not sufficiently close to each other in the mats. Kumamoto *et al.* succeeded in solving these problems by tailoring "thin cellulose sheets," in which these particles were retained evenly in high yields and exposed to oxygen more efficiently compared with the above-mentioned particles mats. When such iron/cellulose composite sheets were prepared, a dual-polymer system using cationic and anionic polymers as retention agents of the particles was adopted. [18]

As described above, cellulose fiber or inorganic fiber/functional inorganic particle composites will have unlimited potentials as functional and innovative paper sheet materials in future, because functions of the composite are rich in diversity by selecting functional particles. Thus, the functional sheet materials will be promising in the

industrial fields or human societies.

1.4 Cellulose wet wiper sheet disposable in toilet

Until 20-30 years ago, when the toilet body and the floor in the toilet room except the inside of toilet bowl were wiped and cleaned, dustcloths made from cotton textile were customarily used in general Japanese households by wetting the cloths with some washing agents or water. After wiping, the used dustcloth is thoroughly washed in water, dried and stored somewhere in the toilet room or other living place for the next wiping. In this case, the dustcloth could be used repeatedly for wiping in toilet room until the cloth becomes damaged and broken by repeated use. However, in the cloth once used for toilet-cleaning some germs could increase to some extent, because the cloth is usually dried in the living space between bathroom and living room without being exposed to sunlight. Therefore, keeping such used dustcloths somewhere in the living place is not cleanly, and furthermore, it is hard or stressful for those, who often clean the toilet room, to wash the dirty dustcloth with water in a bucket and to dry it after wiping.

In order to solve such problems, some wiping methods with wet disposable wiping-sheet products which were impregnated with aqueous washing agents, or dry disposable wiping-sheets impregnated with washing agents just before use, were proposed by some manufacturing companies. [24] Though some of these sheets had enough wet strengths for wiping, they were not disposable and flushable "in toilet bowl" (disposable in trash box). Because these sheets were non-wovens consisting of synthetic and thus nonbiodegradable fibers which could not be discharged into sewage line. Other sheets consisted of cellulose fibers bound by water-soluble polymers such as poly (vinyl alcohol) (PVA) and carboxymethyl cellulose (CMC) in order to make the sheets flushable in toilet. However, such sheet items had weak wet strengths and were easily breakable "during wet-wiping," even though they were disposable and flushable in toilet. [25]

Therefore, wet-wiping sheets "ultimately satisfying enough wet strength in wiping and disposable and flushable properties in toilet bowl," had been desired by those who wanted to wipe and clean the toilet room "easily and firmly."

In 1990, such cellulose wet wiper sheets disposable and flushable in toilet was developed by Kao Corporation. This wet wiper sheet has trade off physical properties, i.e. the sufficient wet strength in wiping (more than 5 Nm g^{-1}) and the water -disintegrability in toilet bowl after use (Figure 1.4). Water-disintegrability is an opposite nature to wet strength of cellulose sheets, the latter of which is required for tissue paper, paper towel, container boards, bank notes, etc (Figure 1.3). Though many patents to manufacture wet wiping sheets disposable in toilet water have been reported,

detailed mechanisms of wet strength development and improvement of water-disintegrability of the wet wiping cellulose sheets and interactions between the sheet components in the presence of impregnation liquids have not been examined yet. [26-29]
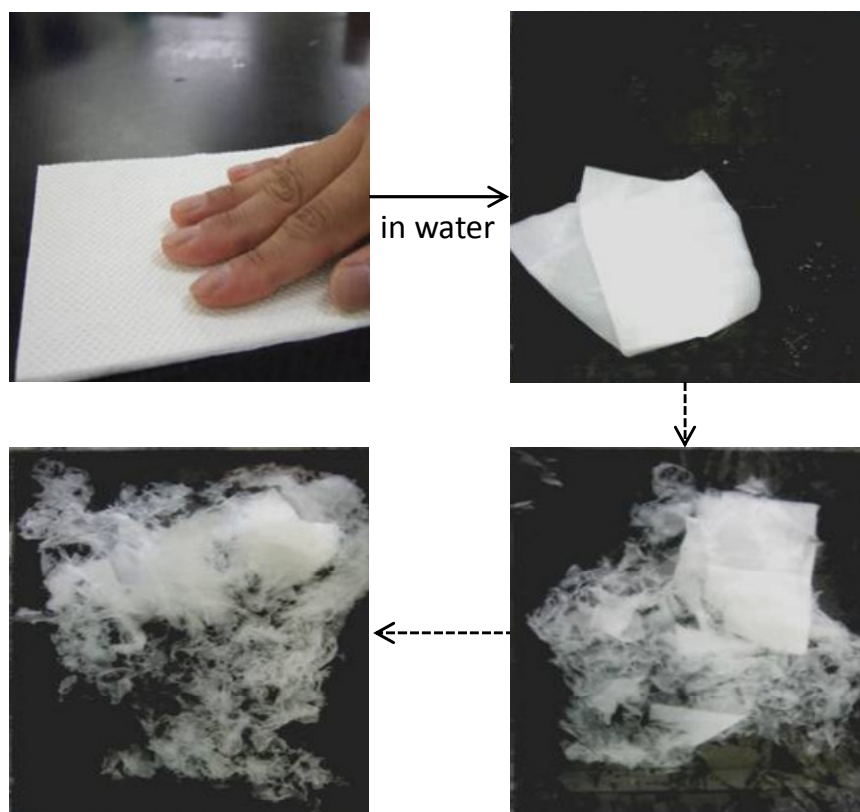
Figure 1.4 Photograph of a wet cellulose wiper sheet with sufficient strength in use, and those of partly disintegrated sheets to fibers or flocs with time after soaking and stirring in water.

  Empirically, it is known that cellulose sheets prepared from partially carboxymethylated cellulose (CMC) fibers have sufficient water-disintegrability more than cellulose sheets without any other chemical modification or additives, whereas sufficient wet strength of the CMC sheets in use cannot be expected. During a research and development project of wet disposable wiping sheets, we deduced that CMC-rich cellulose sheets may have potential to increase wet strength to a certain level by designing the impregnation liquid (water-based detergents) composition. According to Kao's patents, the impregnation liquid basically consists of water, water-soluble organic solvents such as ethanol and/or glycols, divalent metallic ions such as magnesium ion, calcium ion, and zinc ion as the counter ion of carboxyl groups of CMC. [26-28] CMC is

insoluble in pure alcohols, and it forms precipitate in concentrated aqueous calcium chloride solution. [30-33] Therefore, in wiping, insolubilization of CMC in the sheets, by containing alcohols (and/or glycols) and divalent metallic ions in the impregnation liquid, may lead to the conservation of cellulose fiber-binding property of CMC and result in the wet strength development of the sheets. On the other hand, when the sheets are flushed in toilet, solubilization of CMC may be promoted by diluting the concentrations of alcohols and divalent ions and result in the disintegration of the sheets (water-disintegration). However, these matters mentioned above are completely speculative, and detailed mechanisms of wet strength development and improvement of water-disintegrability of the sheets have not been clarified and analyzed from the scientific view.

Two principle procedures have been reported so far to retain anionic CMC molecules on anionic cellulose fibers and sheets. One is irreversible adsorption of CMC molecules with low degrees of substitution on cellulose fibers in specific ways. [34-38] Significant amounts of anionic carboxymethyl groups can be attached to cellulose fibers by these techniques, although the adsorbed amounts of CMC were less than 1.5% on dry weight of the cellulose. Another procedure is so-called dual polymer systems, in which a cationic polymer is used as the retention aid or fixing agent of anionic CMC molecules in papermaking process. By selecting a suitable cationic retention aid, anionic CMC molecules can be efficiently fixed on anionic cellulose fibers by electrostatic interactions, and consequently retained on cellulose sheets by formation of polyion complexes in papermaking process. Such cationic/anionic dual polymer systems have been developed and used to improve fines and filler retentions and/or de-watering performance by forming suitable flocs in high-speed paper machines to produce printing and writing grades. [39-46]

The dual polymer systems are known to be effective also in retention of inorganic powder-like functional particles such as zeolite, iron powders and titanium oxide (photocatalyst) in sheets as described in section 1.3. [13], [16-19] When the weight ratios of the inorganic powders in the sheet components are relatively high, poly(diallyldimethylammonium chloride) (PDADMAC), cationic poly(acrylamide) (C-PAM) and poly(amideamine-epichlorohydrin) (PAE) resin have been predominantly used as the cationic polymers in the dual systems. However, the addition levels of cationic/anionic polymers are generally lower than 0.5% on dry weight of cellulose pulps. In this study, in contrast, relatively large amounts of CMC (>3%) are targeted to be retained in cellulose sheets for wet wiping sheets, which is intrinsically different from the conventional dual polymer systems in papermaking.

In preliminary experiments, cationic surfactants or cationic starches were able to retain CMC molecules to some extent, but no wet strengths appeared on the CMC-containing sheets even if ethanol was used as the impregnation liquid. When PAE resin or aluminum sulfate was used as the cationic retention aid, sufficient wet strength appeared on the sheets but water-disintegrability of the sheets was quite poor. After numerous try and error experiments, we found that one of polymethacrylate esters or PDADMACs containing a quaternary ammonium salt structure in every repeating unit had sufficient retention ability of CMC and wet strength, when ethanol-containing impregnation liquid was used.

1.5 Objective and outline of this study

As mentioned in section 1.4, we deduced that CMC-rich cellulose sheets may have potential to increase in wet strength to a certain level by designing counter ions of carboxyl groups of CMC and/or ethanol is used as one of the components in the impregnation liquid containing water-based detergents. It is hypothesized that some interactions between the CMC-rich cellulose sheet and components in the impregnation liquid bring about the trade-off function; the wet strength in wiping and the water-disintegrability in disposing and flushing the sheets in toilet bowl. Such sheet materials after the liquid soaking treatment can be categorized as "the environmental-responsive functional sheets or intelligent sheets."

In this study, structures of CMC and cationic polymer molecules in cellulose sheets prepared using a papermaking technique by dual polymer systems are made clear by soaking treatments in ethanol/CaCl$_2$-containing solutions. Performances as wet wiper sheets of the composite sheets are scientifically evaluated in terms of strength and water-disintegrability. Retention behavior of polyion complexes formed between carboxymethyl cellulose and cationic polymer molecules in CMC-rich cellulose sheets for wet wiper are studied in terms of colloidal science. Finally, influence of chemical structures of various anionic polysaccharides in place of CMC on wet strength and water-disintegrability of cellulose sheets is investigated. Furthermore, cationic and anionic polymers and cellulose fiber used in sheet-making are characterized in order to analyze physical properties of cellulose sheets for future development of innovative materials or items.

The outline of this study is as follows.

(1) Characterization of polymers and cellulose fiber used in sheet-making (Chapter 2).
(2) Mechanisms for the carboxymethyl cellulose-containing cellulose sheets to have

wet strengths and water-disintegrability (Chapter 3).

(3) Establishment of determination methods of polymer contents in cellulose sheets (Chapter 4).

(4) Retention behavior of polyion complexes formed between carboxymethyl cellulose and cationic polymer molecules in cellulose sheets for wet wiper (Chapter 5).

(5) Influence of chemical structures of anionic polysaccharides on wet strength of cellulose sheets prepared by dual polymer system / Part I: Degree of substitution (DS) of carboxymethyl cellulose (Chapter 6).

(6) Influence of chemical structures of anionic polysaccharides on wet strength of cellulose sheets prepared by dual polymer system / Part II: Distribution of carboxyl groups and chemical structures of main chains (Chapter 7).

(7) Summary (Chapter 8).

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Chapter 2

Characterization of polymers and cellulose fiber used in sheet-making

2.1 Introduction

In this chapter, characteristic data and characterization methods of polymers and cellulose fiber (softwood bleached kraft pulp) used in sheet-making are described in detail.

2.2 Materials and methods

2.2.1 Materials

2.2.1.1 Poly[*N,N,N*-trimethyl-*N*-(2-methacryloxylethyl)ammonium chloride)

Poly[*N,N,N*-trimethyl-*N*-(2-methacryloxylethyl)ammonium chloride] (PTMMAC, Figure 2.1), which was used in cellulose sheet-making as the cationic retention aid of anionic polymers, was synthesized from TMMAC monomer (Mitsubishi Rayon Co., Japan) and purified 2,2'-azobis-2-amidinopropane (V-50) (Wako Pure Chemicals Co., Japan) as the reaction initiator in water at 70 °C for 6 h under nitrogen atmosphere by radical polymerization. [1), 2)] Details of the reaction scheme and procedure are shown in Figures 2.2 and 2.3. Degree of polymerization (DP) was controlled by adjusting the molar ratio of TMMAC monomer and the initiator. The reaction mixture was poured into 2-propanol, and PTMMAC thus obtained as a precipitate was washed thoroughly with 2-propanol by filtration. The PTMMAC solid was dissolved in water, and then freeze-dried. Detail characteristics of PTMMAC are described later.
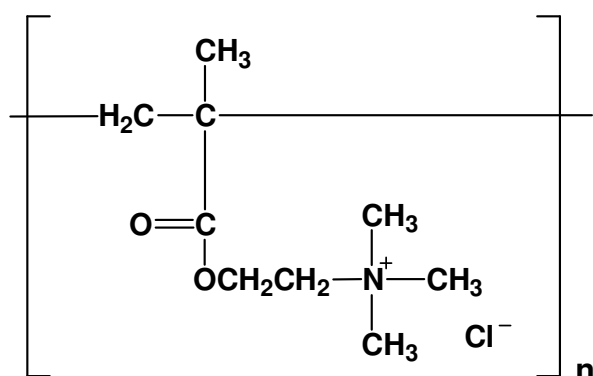
Figure 2.1 Chemical structure of poly[*N,N,N*-trimethyl-*N*-(2-methacryloxyethyl) ammonium chloride] (PTMMAC).
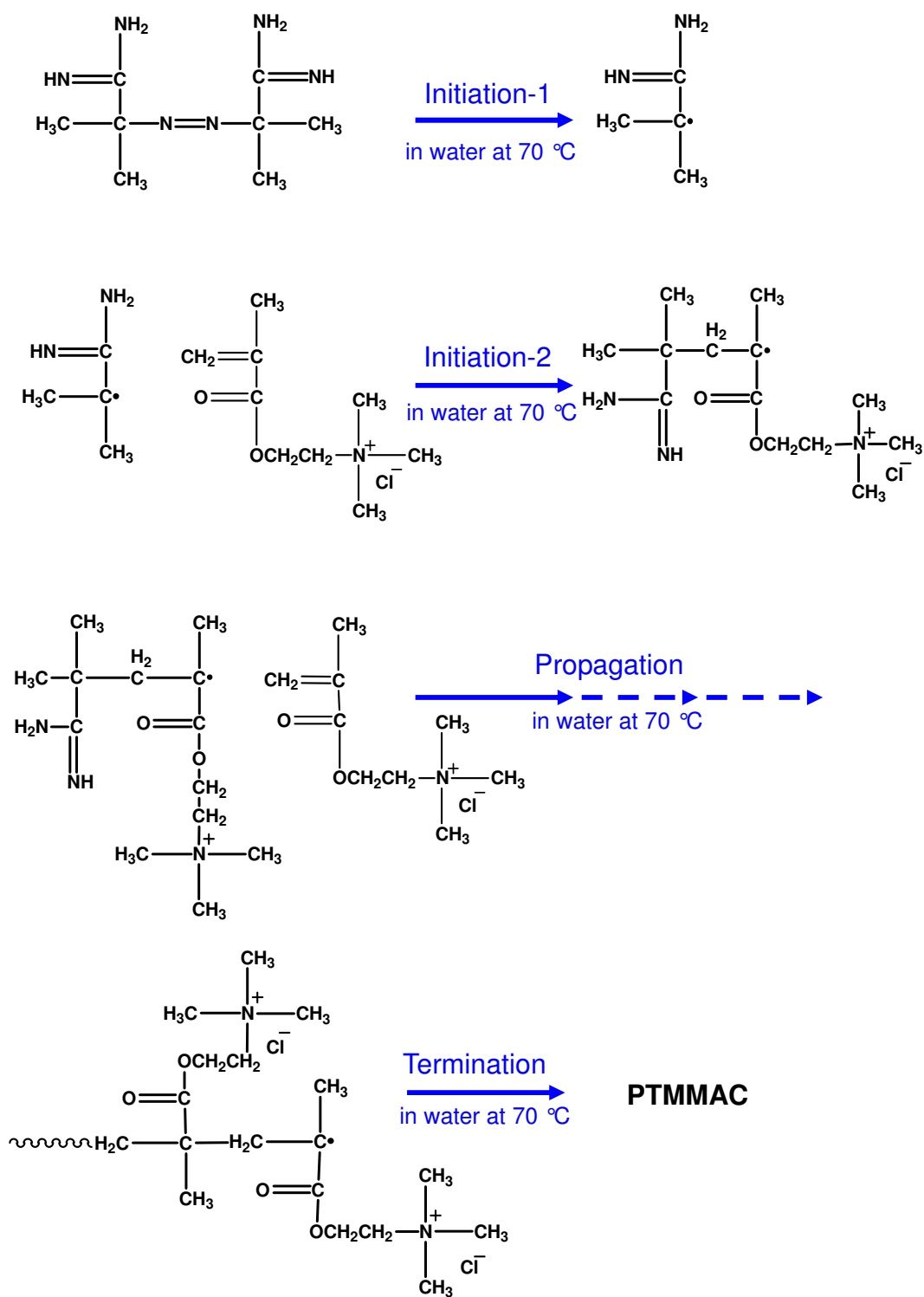
Figure 2.2 Radical polymerization of PTMMAC.
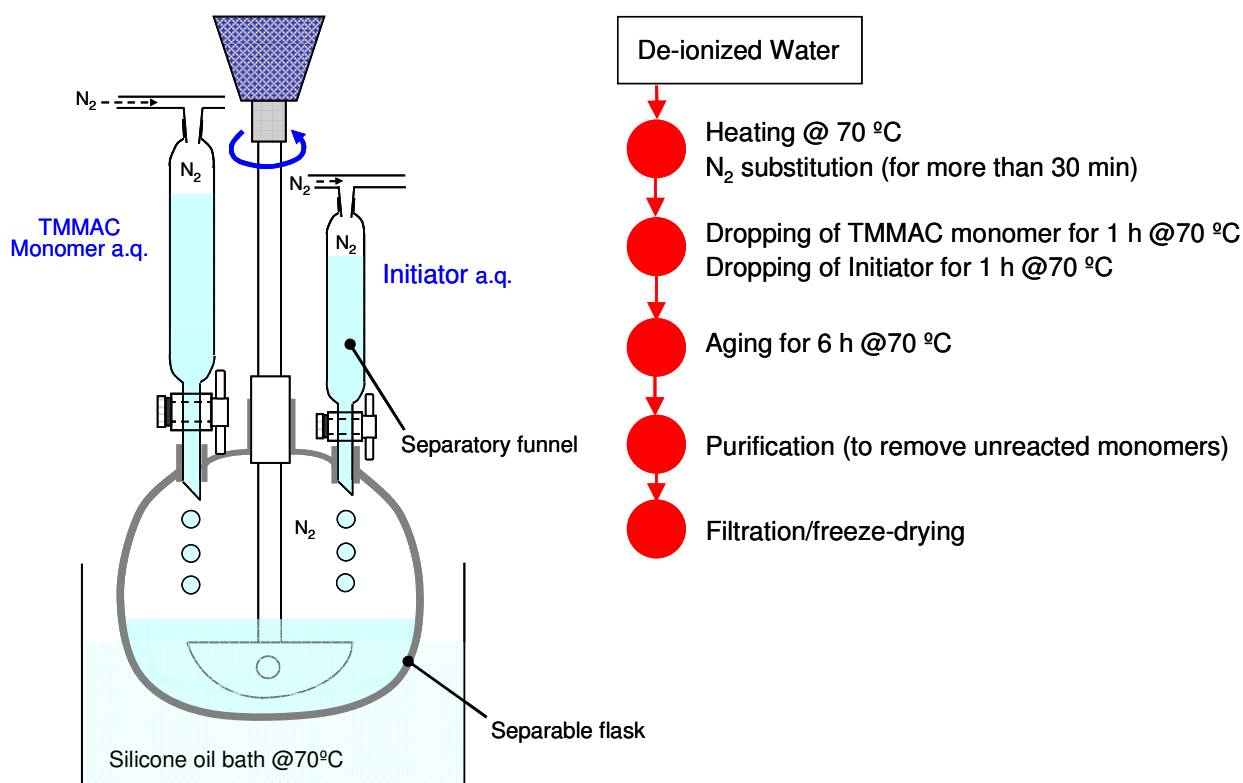
Figure 2.3 Radical polymerization apparatus and procedure for preparation of PTMMAC.

2.2.1.2 Carboxymethyl cellulose

Sodium carboxymethyl cellulose (CMC, Figure 2.4) is an anionic cellulose derivative used in various industrial fields as dispersing and flocculating agent, adhesive, humectant and thickner [3]. As the CMC samples used in this study, commercial and salt-free sodium CMCs with various degrees of substitution (DS) were kindly provided by Daiichi-Kogyo Seiyaku Co., Ltd. Detailed characteristics of CMC are described later.
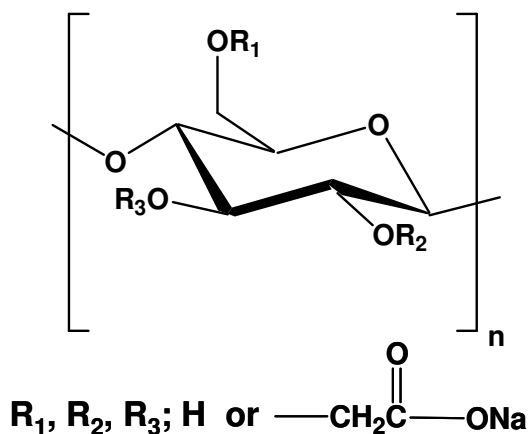
Figure 2.4 Chemical structure of sodium carboxymethyl cellulose (CMC).

2.2.1.3 Alginic acid (Alginate)

Sodium alginate (ALG, Figure 2.5) is a well known copolyuronate isolated from brown seaweeds and certain bacteria, which consists of 1,4-linked anhydro-β-D-mannuronate (M) blocks and 1,4-linked anhydro-α-L-guluronate (G) blocks, forming MG repeated blocks. [4), 5)] ALG is widely applied to food and pharmaceutical materials. ALG used in this study was purchased from Wako Pure Chemicals Co., Japan. Detailed characteristics of ALG are described later.
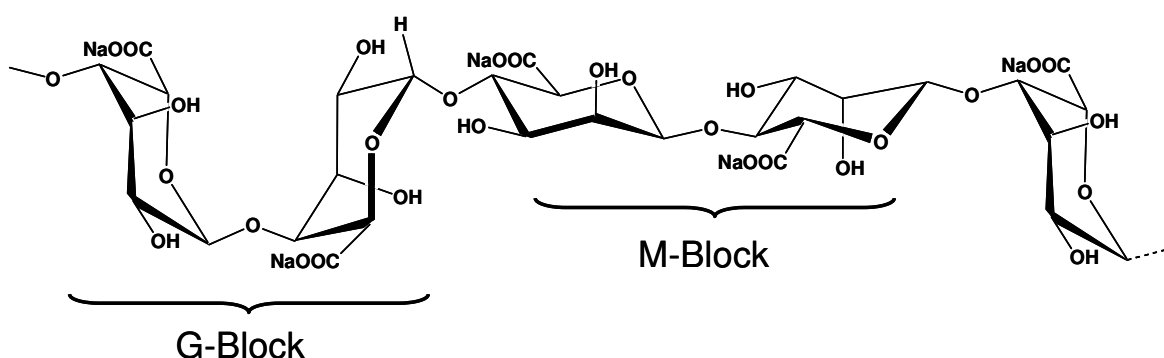
Figure 2.5 Chemical structure of sodium alginate (ALG).

2.2.1.4 Sodium β-1,4-polyglucuronate (Sodium cellouronate)

In our group, sodium β-1,4-polyglucuronate (Sodium cellouronate, CUA, Figure 2.6) was obtained by TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical)-mediated oxidation of regenerated and mercerized celluloses at room temperature, and CUA is a water-soluble polyuronate. [6)] CUA also could be obtained from liquid NH_3-treated native celluloses, [7)] and ball-milled native celluloses [8)] at room temperature. CUA is both biodegradable and metabolizable by microorganisms in nature, and is a promising new polyelectrolyte obtained from biomass. [9), 10), 11)] Futhermore, CUA can be obtained from inedible biomaterials such as cotton and wood, so that, it is beneficial for chemical industry to use abundantly present bioresources. However, CUAs prepared by TEMPO-mediated oxidation at alkaline condition: pH 10-11, have low DP, and the weight-average DP (DP_w) of the CUAs ranges from 40 to 190. [8), 12)] Such CUA with low DP_w is not appropriate as the paper strength additive. In order to obtain CUA with higher DP_w than 300, 4-acetoamido-TEMPO-mediated oxidation at weak acidic or neutral condition: pH 4.8-5.8 was applied to a regenerated cellulose, and the CUA with higher DP_w than 300 could be successfully prepared (Figure 2.7). [13)] Detailed characteristics of CUA are described later.
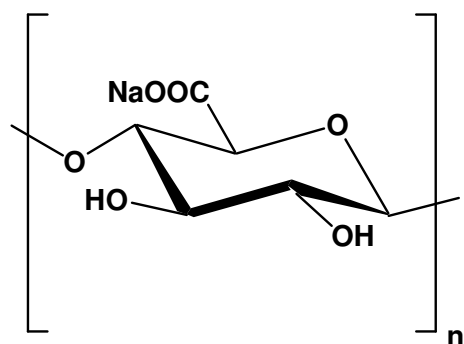
Figure 2.6 Chemical structure of sodium β-1,4-polyglucuronate (CUA).
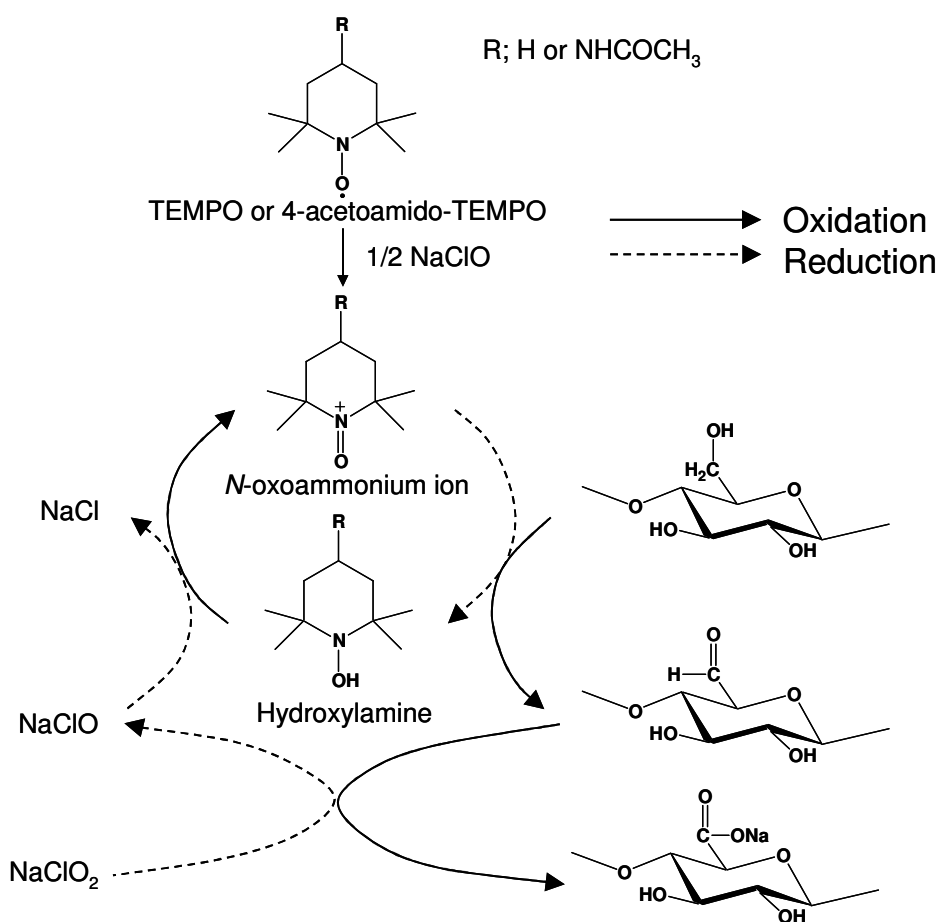
Figure 2.7 Oxidation of C6 primary hydroxyl groups of cellulose by TEMPO-derivative/NaClO/NaClO$_2$ system in water at pH 3.5-6.8.

2.2.1.5 Cellulose fiber

A commercial softwood bleached kraft pulp without beating (750 mL Canadian Standard Freeness) was filtered with tap water on a 150-mesh wire screen to remove

fines fraction, and used as the cellulose fiber in sheet-making. The concentration of the cellulose fiber slurry was adjusted to 10% with water, and was stored at 5 ℃.

2.2.2 Characterizations of the polymers and cellulose fiber

2.2.2.1 Carboxyl contents of anionic polymers and cellulose fiber, and electric charge densities of all materials including PTMMAC

  Carboxyl contents of anionic polymers (CMC, ALG, and CUA) and cellulose fiber (Softwood bleached kraft pulp) were determined by the electric conductivity titration method. [14] In the case of anionic polymers, an accurate amount anionic polymer (1.0 g) was completely dissolved in water (100 mL). 10 mL of the solution was added to water (60 mL) and stirred in 100 mL vessel. Then 1M hydrochloric acid (HCl) aqueous solution was added to the polymer solution to adjust the pH value to 2.0. A 0.08N sodium hydroxide (NaOH) aqueous solution was added at a rate of 0.1 mL min^{-1} up to pH 11 using an auto-titrator (AUT 501; TOADKK, Japan). The values of electric conductivity and pH were recorded with pH/ION/EC/DO meter (MM-60R; TOADKK, Japan) during titration. In the case of cellulose fiber, a dried cellulose (0.3 g) was sufficiently dispersed in water (60 mL) and then 0.1M HCl solution was added to the pulp slurry to set the pH value in the range of 2.0-2.5. A 0.04N NaOH solution was added in the same way as anionic polymer solutions were titrated. Carboxyl contents of anionic polymers and cellulose fiber were determined from conductivity and pH curves, and expressed as an average value of three measurements. The DS value of each CMC was calculated from the carboxyl content determined by the electric conductivity titration. Detail data of carboxyl contents are listed in Table 2.1.

  The electric charge densities (meq. g^{-1}) of catinic polymers (PTMMAC), anionic polymers (CMC, ALG, and CUA), and cellulose fiber were measured by the polyelectrolyte titration method. [14], [15] In the case of cellulose fiber, an accurate amount of cellulose (0.050 g) was sufficiently dispersed in water (20 mL), and the PDADMAC solution of 0.5 meq. L^{-1} (20 mL) was added to cellulose slurry. After stirring for 1 h to reach adsorption equilibrium, the supernatant was separated by filtration, and adjusted to 100 mL by adding water. 10 mL of this filtrate was collected and subjected to the back-titration with 0.1 meq. L^{-1} poly(vinylsulfate, potassium salt) (PVSK) to detect the 0 mV point using an automatic charge analyzer (PCD-03, BTG Mütek GmbH, Germany) in order to determine the amount of PDADMAC remaining in the filtrate. The negative electric charge density of cellulose fiber due to carboxyl groups was calculated from the amount of PDADMAC adsorbed on the cellulose fiber surface, assuming that the polyion complexes were formed between carboxyl groups on

cellulose fiber surface and cationic groups of PDADMAC at 1:1 molar ratio. Three measurements were carried out for determination of each electric charge density, and the average results were reported. The electric charge densities of PTMMACs and anionic polymers were measured by the polyelectrolyte titration method used for cellulose fiber. When the electric charge densities of anionic polymers were measured, an accurate amount of an anionic polymer (0.10 g) was sufficiently dissolved in water (100 mL) and diluted to 0.10 mg mL^{-1}. 10 mL of the solution was collected and subjected to the titration with 1 meq. L^{-1} PDADMAC to detect the 0 mV point using the same automatic charge analyzer as described above. The electric charge density of an anionic polymer was calculated from the amount of PDADMAC. In the case of PTMMAC, the measurement procedure was basically similar to the case of anionic polymers except using 1 meq. L^{-1} PVSK used as the standard solution for titration. Detailed data of charge densities are listed in Table 2.1.

2.2.2.2 Degrees of polymerization and conformations of the polymers

Molecular weight parameters such as weight-average and number-average degrees of polymerizations (DP$_w$ and DP$_n$) of CMC, ALG, CUA and PTMMAC were obtained using a size-exclusion chromatograph with a multi-angle laser-light scattering system (SEC-MALLS) according to previously reported methods (Figure 2.8). [16), 17)] 0.1M sodium nitrate (NaNO$_3$) aqueous solution was used as an eluent for CMC, ALG and CUA, and 0.1M NaNO$_3$, and 0.5M acetic acid aqueous solution for PTMMAC. The SEC-MALLS system consisted of an on-line degasser (DGU-12A, Shimadzu, Japan), a high-pressure pump (LC-10ADVP, Shimadzu), a stainless steel inline filter with a 0.1 µm polytetrafluoroethylene (PTFE) membrane (Millipore, U.S.A.), a automated sampler injector (SIL-20A, Shimadzu), a column oven (CTO-10ACVP, Shimadzu), a pre-column filter with a 0.5 µm stainless steel frit (A-310; Upchurch Scientific, USA), a guard column (SB-G; Shodex, Japan), a SEC column packed with polyhydroxymethacrylate gel (SB-806M; Shodex), a MALLS detector (DAWN EOS, λ=690 nm; Wyatt technologies, U.S.A.) and a refractive index (RI) ditector (RID-10A; Shimadzu). Data acquisition and processing were carried out by using the ASTRA IV software (Wyatt Technologies). SEC conditions were as follows: the sample concentration was 0.1 mg/mL, injection volume was 100 µL, flow rate was 0.50 mL min^{-1}, and the column temperature was 40 ℃. The detector cells of MALLS and RI were kept at room temperature. Before injection, sample solutions were filtered through a 0.2 µm hydrophilic PTFE disposable membrane (Millex-LG; Millipore). Specific refractive index increments (dn/dc) of solutions prepared at 0.1-0.5 mg mL^{-1} were determined at λ=690 nm using an Optilab interferometric refractometer and the attached

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- Molecular mass by MALLS
- Radius of gyration by MALLS (>10nm)
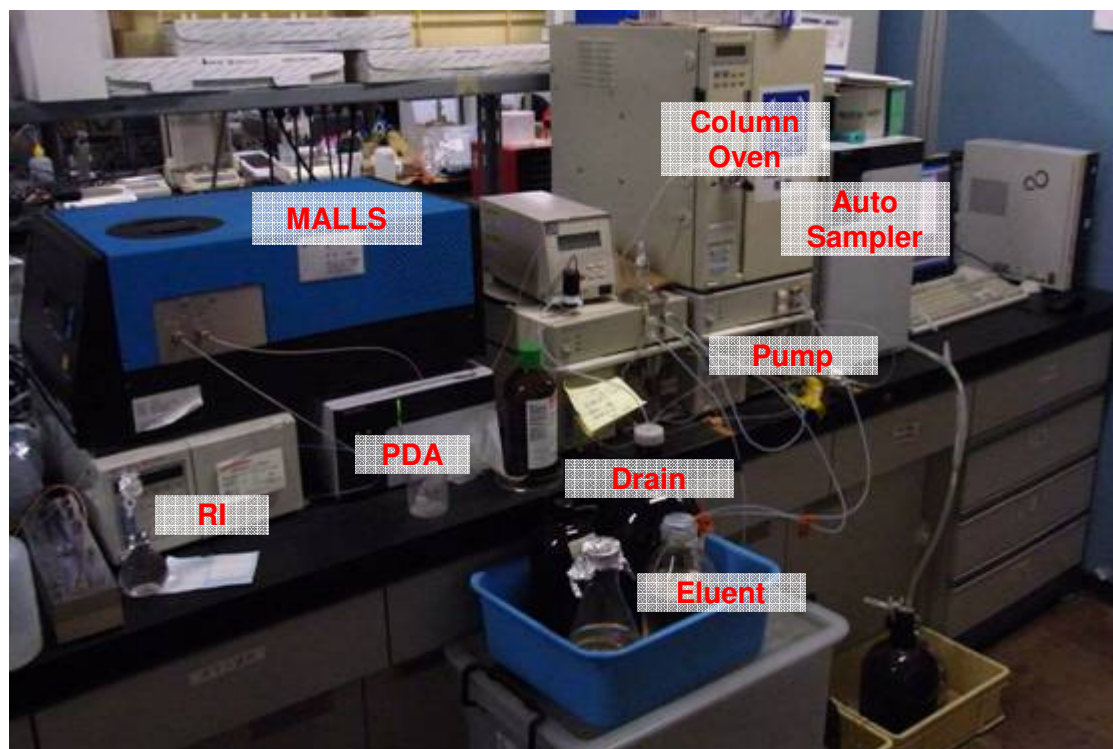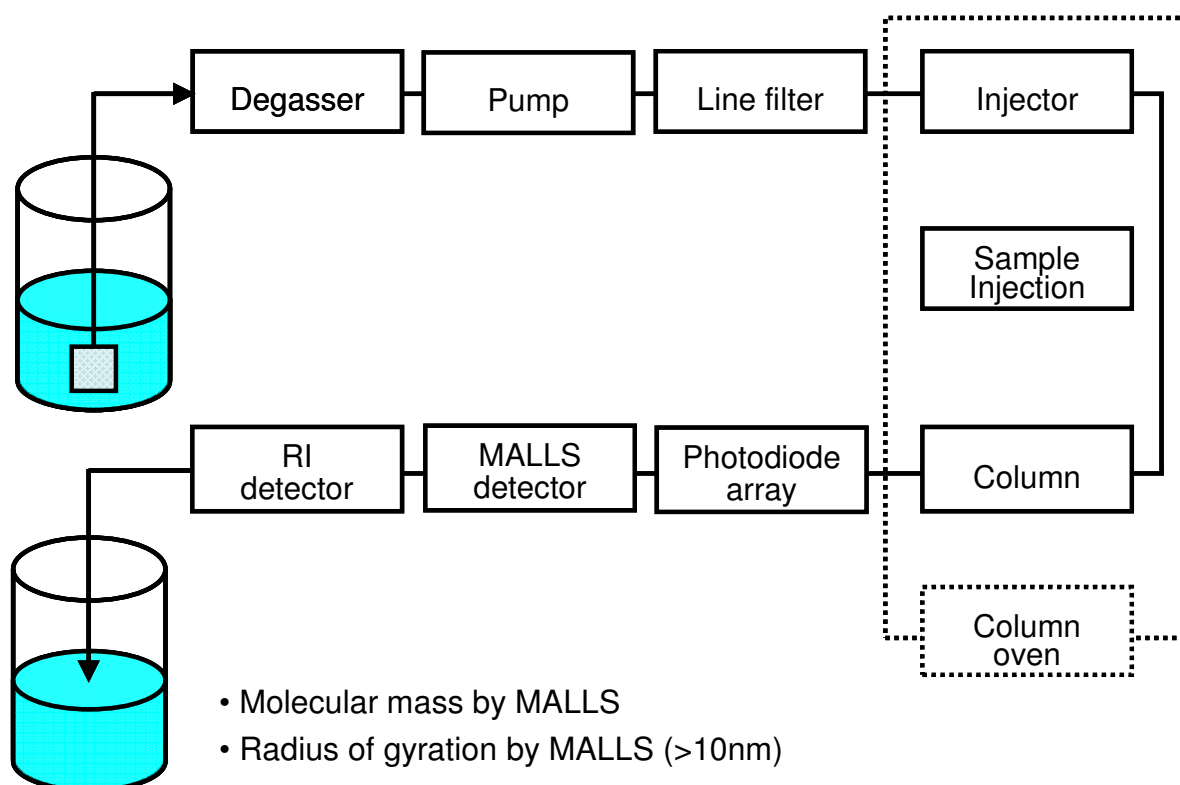
Figure 2.8 A schematic picture and a photograph of the SEC-PDA-MALLS system used for the measurement of molecular weight parameters of polymers.

DNDC software (Wyatt Technologies). The dn/dc values of PTMMAC, CMC, ALG, and CUA used in this study were 0.166, 0.154, 0.155, and 0.125 mL g^{-1}, respectively. [12), 13)]

2.3 Results and discussions

2.3.1 Carboxyl contents of anionic polymers and cellulose fiber, and electric charge densities of all materials including PTMMAC

Fundamental characteristics of the PTMMAC, CMC, ALG, CUA and cellulose fiber used in sheet-making are listed in Table 2.1. Because the cationic charge densities of PTMMACs determined by polyelectrolyte titration method (4.74-4.85 meq. g^{-1}) were close to the values calculated from their molecular formula in Figure 2.1 (4.82 meq. g^{-1}), cationic and anionic groups of PTMMAC and PVSK molecules, respectively, form a paired structure mostly at the molar ratio of 1:1 in the PTMMAC/PVSK polyion complexes during the titration. On the other hand, the anionic charge densities of ALG and CUA calculated from their molecular formulas (Figures 2.5 and 2.6), which were close to the carboxyl contents determined by the conductivity titration method, but were clearly higher than those determined by the polyelectrolyte titration method. The carboxyl contents of CMCs were also higher than the anionic charge densities of those similarly determined. For example, the carboxyl content of the CMC (CMC-2 in Table 2.1) was 4.03 mmol g^{-1}, which was determined by the conductivity titration method, but was clearly higher than the anionic charge density (3.54 meq. g^{-1}) determined by the polyelectrolyte titration method. The heterogeneous distribution of carboxymethyl substituents along one CMC molecule or the difference of molecular chain backbones between CMC, ALG, CUA and PDADMAC may have caused such difference in the values between charge densities and carboxyl contents.

2.3.2 Degrees of polymerization and radii of gyration of polymers

Figures 2.9 (a), (b) and (c) show SEC elution patterns and the corresponding molecular mass (MM) plots of CMCs, ALG, and CUA, respectvely. In Figure 2.9 (c), the SEC pattern and MM plot of CUA with a low DP obtained by TEMPO-mediated oxidation at pH 10 are shown as a reference. [6)] SEC elution patterns and MM plots of PTMMACs with various molecular weights are shown in Figure 2.10. Figures 2.11, 2.12, and 2.13 depict conformation plots, i.e. z-root mean square radii of gyration ($<S_Z^2>^{1/2}$) versus molecular weight obtained by SEC-MALLS analyses for CMC, ALG, CUA, and PTMMAC, respectively. From MM plots of all polymers, size exclusion of polymers by SEC column was appropriately accomplished except the CMC with DS 0.49 and the CUA prepared by TEMPO-mediated oxidation at pH 5.8. In the SEC elution pattern of
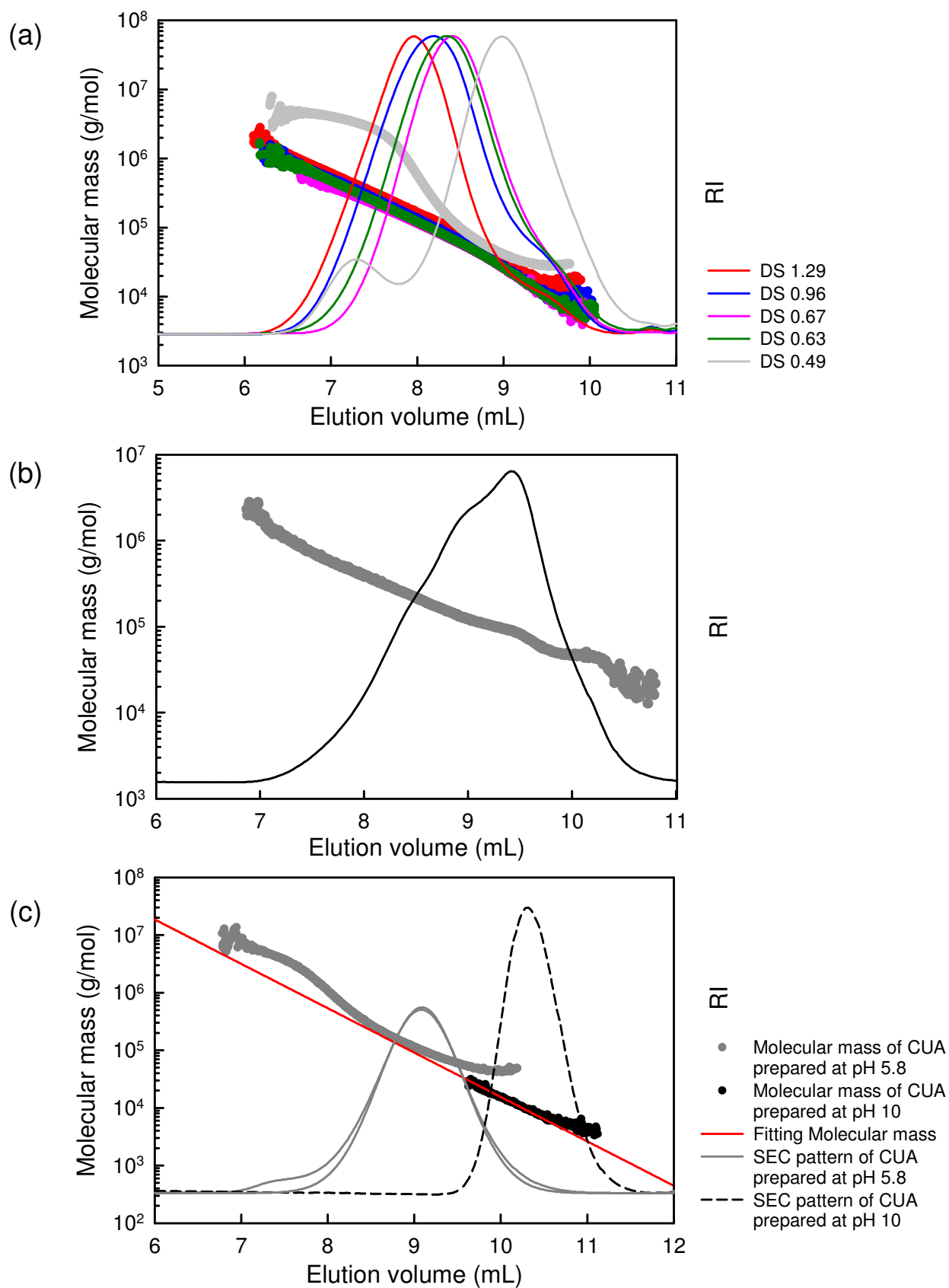
Figure 2.9 SEC elution patterns and the corresponding molecular mass plots of (a) CMCs, (b) ALG, and (c) CUA used for cellulose sheet-making.
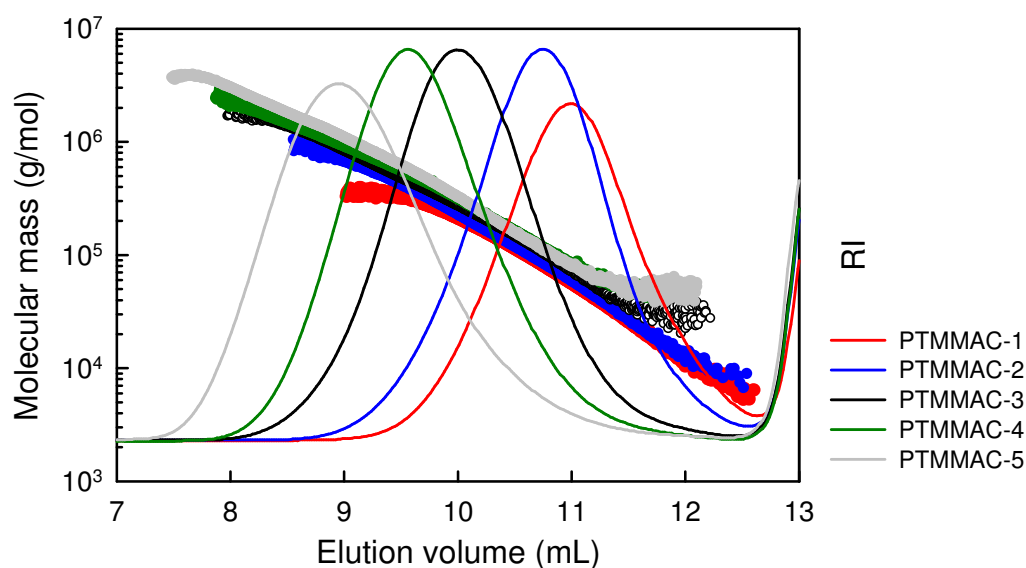
Figure 2.10 SEC elution patterns and the corresponding molecular mass plots of PTMMACs used in cellulose sheet-making.
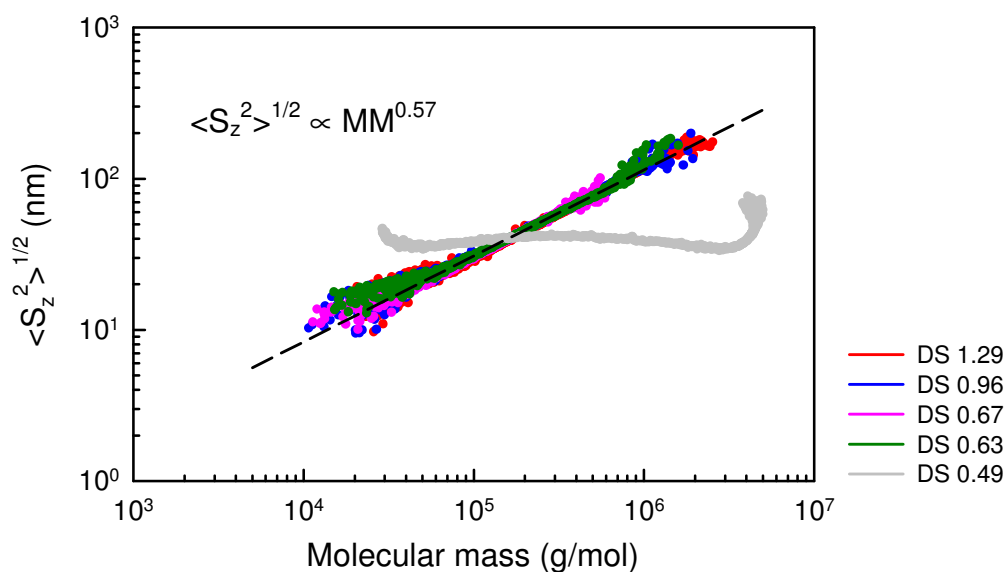
Figure 2.11 Conformation plots of CMCs.

the CMC with DS 0.49 and the CUA obtained by TEMPO-mediated oxidation at pH 5.8, there were minor peaks corresponding to molecular weights higher than those of major peaks (Figures 2.9 (a) and (c)). These minor peaks were due to molecular aggregates or incompletely dissolved components. [13), 16)] Because of these minor peaks, DP values of the CMC with DS 0.49 and the CUA obtained at pH 5.8 could not be determined exactly. However, the CUA, obtained at pH 5.8, was almost pure CUA molecules as the major component (corresponding to the major peak in Figure 2.9 (c)), as reported by Hirota *et*

al. [13] Thus, the relatively reliable DP value of the CUA, obtained at pH 5.8, can be estimated by extrapolating MM plot of the CUA with a low DP (obtained by TEMPO-mediated oxidation at pH 10) to the smaller elution volume and by dividing SEC pattern into the major peak and minor peak with Gaussian fitting (Figure 2.9 (c)).

According to the scaling concept of polymer solution, CMCs except that with DS 0.49 and ALG have random coil conformations in the eluent, because $<S_z^2>^{1/2}$ data plots of CMCs and ALG were proportional to those of $MM^{0.50-0.60}$ (Figures 2.11 and 2.12). [18] All conformation plots of CMCs except that with DS 0.49 were almost on the same line (Figure 2.11). On the other hand, the CMC with DS 0.49 and the CUA prepared at pH 5.8 have the conformations indicating intra- and/or inter-molecular aggregates or imcompletely dissolved components. [16] Meanwhile, all PTMMACs have random coil conformations, because $<S_z^2>^{1/2}$ plots of PTMMACs were proportional to those of $MM^{0.69}$ (Figure 2.13).
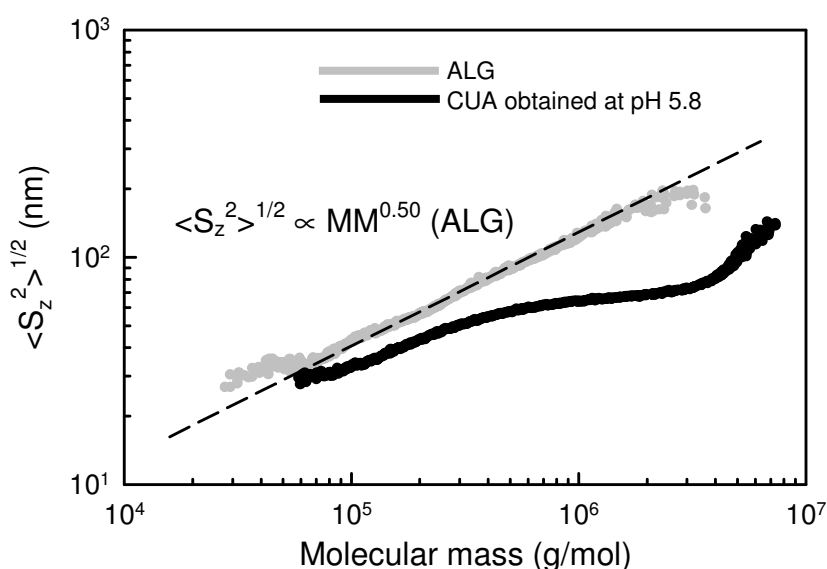
Figure 2.12 Conformation plots of alginate (ALG) and β-1,4-polyglucuronate (CUA).

Consequently, polymers used in the following chapters basically have random coil conformations in the aqueous eluent, therefore, in sheet-making process, these polymers probably have similar conformations, because the electric conductivity of the water (tap water) used in sheet-making is 0.25 mS cm^{-1}, corresponding to 0.002M NaNO$_3$ aqueous solution, was smaller than that of the eluent used in SEC-MALLS, corresponding to 0.1M NaNO$_3$ aqueous solution. Detailed data of DP$_w$, DP$_w$/DP$_n$, and $<S_z^2>^{1/2}$ are listed in Table 2.1.
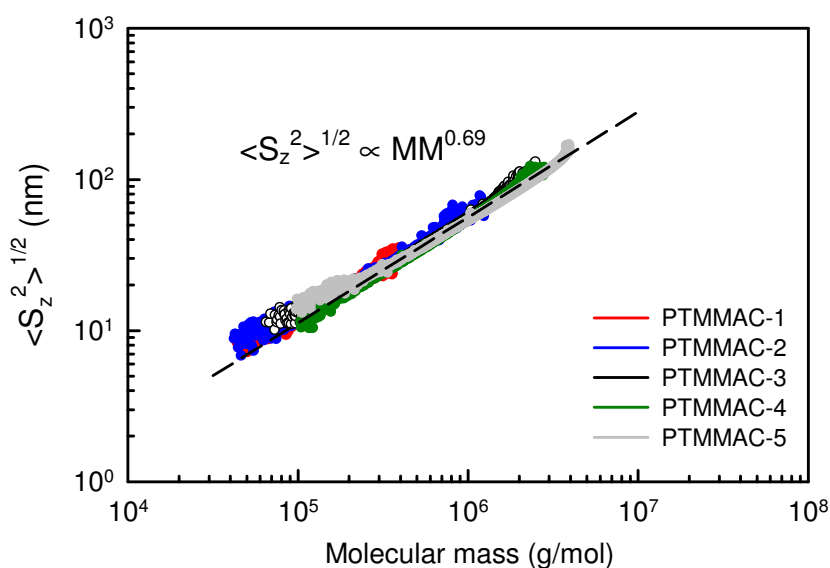
Figure 2.13 Conformation plots of PTMMACs.

Table 2.1 Characteristics of PTMMACs, anionic polymers, and cellulose fiber used in sheet-making.

Sample	Degree of substitution[a]	DP_w	DP_w/DP_n	$<S_z^2>^{1/2}$ (nm)[b]	Charge density (meq. g^{-1})	Carboxyl content (mmol g^{-1})[c]
PTMMAC-1	–	342	2.2	19	4.75	–
PTMMAC-2	–	540	2.1	25	4.84	–
PTMMAC-3	–	1570	1.9	39	4.83	–
PTMMAC-4	–	2510	1.7	48	4.85	–
PTMMAC-5	–	6450	2.2	83	4.74	–
CMC-1	1.29	840	2.4	70	4.01	4.86
CMC-2	0.96	640	2.8	57	3.54	4.03
CMC-3	0.67	385	2.3	37	2.98	3.09
CMC-4	0.63	486	2.7	48	2.72	2.96
CMC-5	0.49	–	–	–	1.80	2.43
ALG	–	790	1.7	69	4.60	5.09
CUA	–	590	2.2	–	4.24	4.60
Cellulose	–	–	–	–	0.007	0.06

[a] Calculated from carboxyl content

[b] Radius of gyration   [c] Determined by electric conductivity titration method

2.4 Summary

In this chapter, fundamental characterizations of polymers and cellulose fiber used in sheet-making were conducted by titration methods and SEC-MALLS analyses in detail.

Consequently, almost all the polymers used in this study probably have simple chemical structures, and have random coil conformations in the water (tap water) used in sheet-making process. In order to analyze the retention behaviors of polymers on cellulose fibers in cellulose sheet-making process or the physical properties of the obtained cellulose sheets in terms of colloid science and polymer science in the following chapters, the characteristics of the materials used in this study are quite significant.

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Chapter 3

Mechanisms for the carboxymethyl cellulose-containing cellulose sheets to have wet strengths and water-disintegrability

3.1 Introduction

Water-disintegrable and flushable cellulose sheets have been used as household commodity goods such as toilet paper and some wiping sheets for clearing toilet and bathroom, and uncommonly as printing and writing paper for confidential documents. Water-disintegrability is an opposite nature to wet strength of cellulose sheets, the latter of which is required for tissue paper, paper towel, container boards, bank notes, etc. When cellulose fibers are used as the main component of wet wiping sheets disposable in toilet water after cleaning toilet and bathroom, the trade-off properties, i.e. sufficient wet strength in use and water-disintegrability after use, are required (Figure 1.4 of Chapter 1). Although many patents to manufacture wet wiping sheets disposable in toilet water have been published, detailed mechanisms of wet strength development and improvement of water-disintegrability of the wet wiping cellulose sheets and interactions between the sheet components in the presence of impregnation liquids have not been clarified yet. [1-3]

As described in Chapter 1, during the research and development project of wet disposable wiping sheets, we considered that CMC-rich cellulose sheets may have potential to increase in wet strength to a certain level by designing counter ions of carboxyl groups of CMC and/or ethanol is used as one of the components in impregnation liquid containing water-based detergents. In this study, relatively large amounts of CMC (>3% on dry weight of cellulose fiber) are targeted to be retained in cellulose sheets for wet wiping sheets. As the procedure to retain a large amount of anionic CMC molecules on cellulose fibers and sheets, so-called dual polymer systems, in which cationic polymers are used as retention aids or fixing agents of anionic CMC molecules in papermaking process, were adopted (Chapter 1). [4-5]

In preliminary experiments, cationic surfactants or cationic starches were able to retain CMC molecules to some extent, but no wet strengths appeared on the CMC-containing sheets even ethanol was used as the impregnation liquid. When poly(amideamine-epichlorohydrin) PAE resin or aluminum sulfate was used as the

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cationic retention aid, sufficient wet strength appeared on the sheets but water-disintegrability of the sheets was quite poor. After numerous try and error experiments, we found that one of polymethacrylate esters containing a quaternary ammonium salt structure in every repeating unit had sufficient retention ability of CMC and gave the obtained cellulose sheets both of wet strength and water-disintegrability, when ethanol-containing impregnation liquid was used.

In this chapter, structures of CMC and the cationic polymer molecules in cellulose sheets prepared using a papermaking technique by dual polymer systems are made clear by soaking treatments in ethanol/CaCl$_2$-containing solutions, and performances as wet wiper sheets of the composite sheets are evaluated in terms of strength and water-disintegrability.

3.2 Materials and methods

3.2.1 Materials

A commercial softwood bleached kraft pulp without beating (750 mL Canadian Standard Freeness) was filtered with tap water on a 150-mesh wire screen to remove fines fraction, and used as the cellulose fiber in sheet-making. A sodium carboxymethyl cellulose (CMC, Figure 2.4 in Chapter 2) was kindly provided by Daiich-Kokyo Seiyaku Co., Ltd., Japan, and its DS was 0.96 according to the carboxyl content determined by electric conductivity titration method (Chapter 2). A poly [*N,N,N*-trimethyl-*N*-(2-methacryloxylethyl) ammonium chloride] (PTMMAC, Figure 2.1 in Chapter 2) with DP$_w$ 342 was synthesized by radical polymerization (Chapter 2). [6), 7)] One % (w v^{-1}) solutions of CMC and PTMMAC were prepared with distilled water, and used as additives in sheet-making process. Other chemicals and solvents were of laboratory grade (Wako Pure Chemicals Co., Japan) and used as received. The fundamental characteristics of the CMC, the PTMMAC, and cellulose fiber used in this chapter were evaluated according to the methods using analytical apparatuses such as a size-exclusion chromatograph with a multi-angle laser-light scattering system (SEC-MALLS), the electric conductivity titration method, and the polyelectrolyte titration method (Chapter 2), and are listed in Table 3.1.

3.2.2 Cellulose sheet-making with PTMMAC and CMC

The cellulose fiber (10 g) was suspended in tap water (1 L) under continuous stirring at 300 rpm. The 1% PTMMAC solution (50 mL) was first added to the cellulose slurry. After stirring for 1 min, the 1% CMC solution (50 mL) was then added. Hence, the addition levels of PTMMAC and CMC were both 5% based on the dry weight of the

cellulose. After additional stirring for 3 min, cellulose sheets with a basis weight of 60 g m^{-2} were prepared from the slurry with tap water according to TAPPI Test Method T205 om-88 (2005). The conductivity and pH of tap water used in sheet-making were 0.25 mS cm^{-1} and 7.3, respectively. The wet-pressed sheets were dried at 100 °C for 2 min using a rotary drum-dryer. The cellulose sheets containing PTMMAC and CMC thus obtained were conditioned at 23 °C and 50% relative humidity for more than 1 day.

Table 3.1 Characteristics of PTMMAC, CMC, and cellulose fiber used in sheet-making.

Sample	Degree of substitution[a]	DP$_w$	DP$_w$/DP$_n$	$<S_z^2>^{1/2}$ (nm)[b]	Charge density (meq. g^{-1})	Carboxyl content (mmol g^{-1})[c]
PTMMAC-1	–	342	2.2	19	4.75	–
CMC-2	0.96	640	2.8	57	3.54	4.03
Cellulose	–	–	–	–	0.007	0.06

[a] Calculated from carboxyl content

[b] Radius of gyration   [c] Determined by electric conductivity titration method

3.2.3 Soaking of the cellulose sheets in ethanol-containing solutions

The cellulose sheet (60 g m^{-2}) was cut into strip specimens with 15 mm wide and >150 mm long or to square sheets with 20 × 20 mm, and soaked in mixtures (100 mL) of ethanol, water and calcium chloride with various weight ratios for 30 min. The strip specimens were picked up from the soaking solutions, and immediately subjected to the wet tensile test according to TAPPI Test Method (T 456 om-87, 2001). The amounts of soaking solution adsorbed by the strip specimens ranged from 250 to 300 weight % based on dry weight of the specimens. The square sheet samples were picked up from the soaking solutions, stirred in fresh ethanol (100 mL) for more than 30 min, and washed repeatedly with fresh ethanol and finally with acetone by filtration. After air- and then vacuum-drying, the sheet samples were subjected to determination of nitrogen, calcium and chlorine contents described below.

3.2.4 Analyses

The PTMMAC-N$^+$ contents of cellulose sheets were calculated from their nitrogen contents determined by combustion-type gas-chromatography (FLASH EA1112

NC-analyzer; Thermo Fisher Scientific Inc, US), on the basis of the chemical formula of PTMMAC (Figure 2.1 in Chapter 2). [8] The calcium and chlorine contents of cellulose sheets were determined using an energy-dispersive X-ray (EDX) spectroscope in quantitative mode (EMAX-5770X; Horiba, Japan) attached with a scanning electron microscope (SEM) (S-4000; Hitachi High-Technologies Corp., Japan) at 20 μA for 100 s after osmium coating with OsO_4 gas at 10 mA for 10 s (Neoc, Meiwafosis Co., Ltd., Japan). [9] The cellulose sheet was cut into small pieces and converted to a disk pellet 2 cm in diameter (0.3 g) by pressing at 750 MPa for 1 min. The calcium content of the pellet was determined using a X-ray fluorescence analyzer (XRFA) (MESA-500, Horiba, Japan) with X-ray generation at 15 kV and 500 μA according to a previously reported method. [10-12] The cellulose sheets samples supplied for the specimen were prepared by soaking the sheets in the aqueous liquid containing $CaCl_2$ and washing with ethanol thoroughly in order to remove excess $CaCl_2$ in the sheets without disintegrating. A series of well mixed powders of $CaCl_2$ and microcrystalline cellulose with known weight ratios were converted to pellets, and were used to obtain calibration curves for determination of Ca and Cl contents in the sheets by SEM-EDX and XRFA. Details of determination method of PTMMAC, CMC and Ca^{2+} ions in the sheets are described in Results and discussion section. Bulk analyses of Ca and Cl determination using SEM-EDX and XRFA were carried out on the assumption that these elements were homogeneously distributed in the sheets.

3.3 Results and discussions

3.3.1 Characteristics of PTMMAC and CMC used in sheet-making

Fundamental characteristics of the PTMMAC, CMC and cellulose fiber used in this study are listed in Table 3.1. Because the cationic charge density of PTMMAC determined (4.75 meq. g^{-1}) was close to the value calculated from its molecular formula in Figure 2.1 in Chapter 2 (4.82 meq. g^{-1}), cationic and anionic groups of PTMMAC and PVSK molecules, respectively, become paired mostly at the molar ratio of 1:1 in the PTMMAC/PVSK polyion complexes formed during the charge density determination. The carboxyl content of CMC was 4.03 mmol g^{-1} determined by the conductivity titration method but was clearly higher than the charge density (3.54 meq. g^{-1}) determined by the polyelectrolyte titration method. The heterogeneous distribution of carboxymethyl substituents along one CMC molecule may have caused such difference in the values between charge density and carboxyl content in Table 3.1. [13]

In this chapter, the addition levels of PTMMAC and CMC to cellulose slurries were both fixed to 5% on dry weight of the cellulose. When 1 g cellulose exists in the

PTMMAC/CMC/cellulose slurry subjected to the sheet-making, the amount of cationic groups due to PTMMAC present in the slurry was 0.238 mmol and the total anionic groups originating from CMC and the cellulose surface was 0.209 mmol. Thus, the PTMMAC/CMC/cellulose slurry was set to be slightly rich in cationic groups. Because the surface charge of the cellulose fiber was only 0.007 meq. g^{-1}, all carboxylate groups of CMC should form ammonium salts with PTMMAC, forming polyion complexes. Details of retention mechanisms of PTMMAC and CMC molecules on the cellulose sheets in sheet-making process and their structures of polyion complexes are discussed in Chapter 5 based on PTMMAC and CMC contents of the PTMMAC/CMC/cellulose sheets.

3.3.2 Wet-tensile strength of PTMMAC/CMC/cellulose sheets soaked in EtOH/H$_2$O/CaCl$_2$ solutions

The PTMMAC/CMC/cellulose sheets were soaked for 30 min in either EtOH/H$_2$O/CaCl$_2$ solutions (Solutions A) or EtOH/H$_2$O solutions (Solutions B) with various weight ratios of the components, and the wet tensile strengths were immediately measured without drying (Figure 3.1). Because inter-fiber hydrogen bonds present in the PTMMAC/CMC/cellulose sheets and contributing to sheet strengths should be mostly maintained even by soaking the sheets in solutions rich in EtOH, it was expected that wet strengths increased as the EtOH content of the soaking solutions was increased. When the blank cellulose sheets prepared without PTMMAC or CMC were soaked in the solutions, similar wet strength patterns between Solutions A and B were obtained; wet strengths increased with increasing ethanol content of the soaking solutions. However, the maximum strengths were only about 5 Nm g^{-1} even at 0% H$_2$O. Thus, wet strengths were low for these blank cellulose sheets irrespective of the presence of CaCl$_2$ in the soaking solutions.

When the PTMMAC/CMC/cellulose sheets were soaked in Solutions B, the wet strength of the sheets increased to 26 Nm g^{-1} at 100% EtOH. Hence, the formation of polyion complexes between PTMMAC and CMC molecules in the cellulose sheets explicitly led to the wet strength improvement probably by reinforcing effect of inter-fiber bonds. The wet strength decreased as the H$_2$O content of Solution B was increased, and no wet strengths were detected when 100% H$_2$O was used as the soaking solution.

On the other hand, when the PTMMAC/CMC/cellulose sheets were soaked in Solutions A containing 1 wt % CaCl$_2$ (i.e. 0.090 mmol CaCl$_2$ per gram of the solution), a different wet strength pattern was observed particularly for the Solutions A with EtOH

contents from 60% to 20%. The presence of 1% $CaCl_2$ in the soaking solutions clearly improved wet tensile strengths of the sheets in this range of the EtOH content. When one of Solutions A with various $EtOH/H_2O/CaCl_2$ weight ratios used in the soaking treatment of Figure 3.1 is used as a liquid component containing water-based detergents for wet wiper cellulose sheets, the EtOH content should be kept as low as possible in order to remove the dirt easily in the toilet, but the wet strengths should be >5 Nm g^{-1} for keeping the sheet form in use. In contrast, the wet strength should disappear in 100% H_2O, considering the cases of disposal of the used wiper sheets in toilet water. It was found from the results in Figure 3.1, therefore, that the $EtOH/H_2O/CaCl_2$ solution with the weight ratio of approximately 20:79:1 was preferable to be used as the impregnation liquid to the PTMMAC/CMC/cellulose sheets for wet wipers.
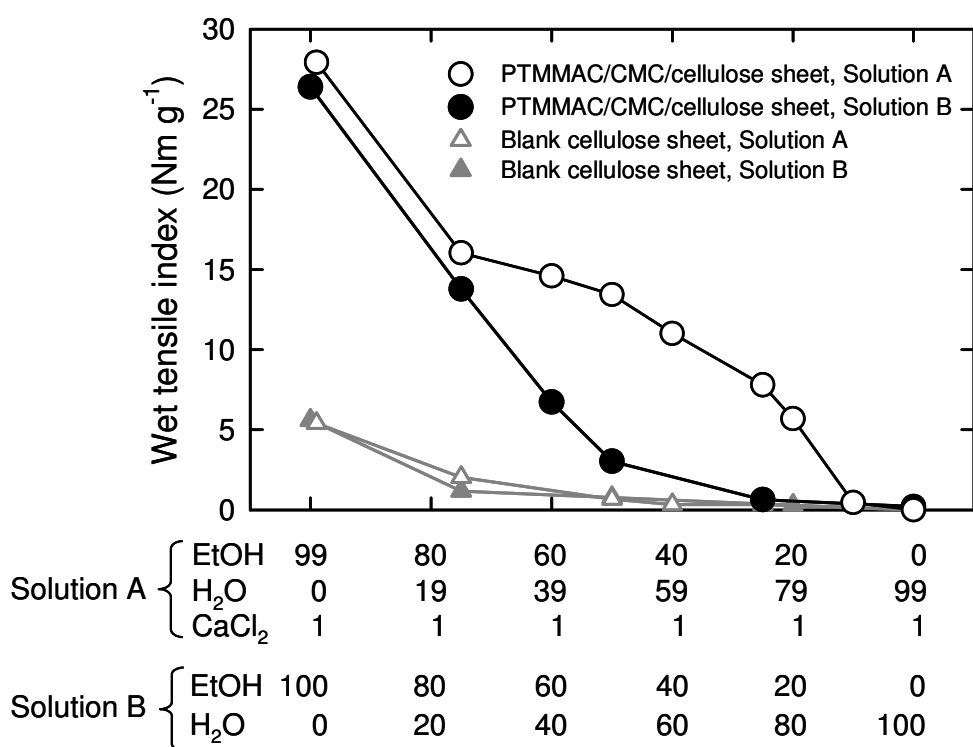
Figure 3.1 Relationships between weight ratios of the soaking solution components and wet tensile strength of the blank cellulose and PTMMAC/CMC/cellulose sheets soaked in the solutions.

3.3.3 Determination of PTMMAC-N$^+$, CMC-COO$^-$ and Ca^{2+} contents in sheets

  The PTMMAC, CMC and calcium contents of the sheets before and after the soaking treatments in Solutions A should be determined in order to explain the mechanism of

wet strength improvement for the PTMMAC/CMC/cellulose sheets in Figure 3.1. Figure 3.2 shows the contents of PTMMAC-N^+ ions in the sheets before and after the soaking treatment in Solutions A with different $EtOH/H_2O/CaCl_2$ weight ratios, were calculated from nitrogen contents of the sheets. Because PTMMAC-N^+ molecules are insoluble in EtOH, almost all PTMMAC-N^+ molecules present in the original PTMMAC/CMC/cellulose sheets remained in the sheets even after soaking in Solutions A with 99% and 75% EtOH contents, and the PTMMAC-N^+ contents in this range were approximately 35.1 mg g^{-1}. The water-soluble PTMMAC-N^+ molecules were prone to be removed as PTMMAC-N^+Cl^- molecules from the sheets as the H_2O content of Solutions A was increased. The PTMMAC-N^+ contents became lower than 2 mg g^{-1}, when the EtOH contents of the soaking solution were lower than 25%. Thus, more than 94% of PTMMAC-N^+ molecules originally present in the PTMMAC/CMC/cellulose sheets were removed from the sheets by soaking in the water-rich solutions. These results indicate that cationic PTMMAC-N^+ molecules, which are present in the original PTMMAC/CMC/cellulose sheets forming polyion complexes mostly with anionic CMC-COO^- molecules, became soluble in water-rich soaking solutions containing $CaCl_2$ by exchanging their counter ions from CMC-COO^- molecules to Cl^- ions during the soaking treatment.
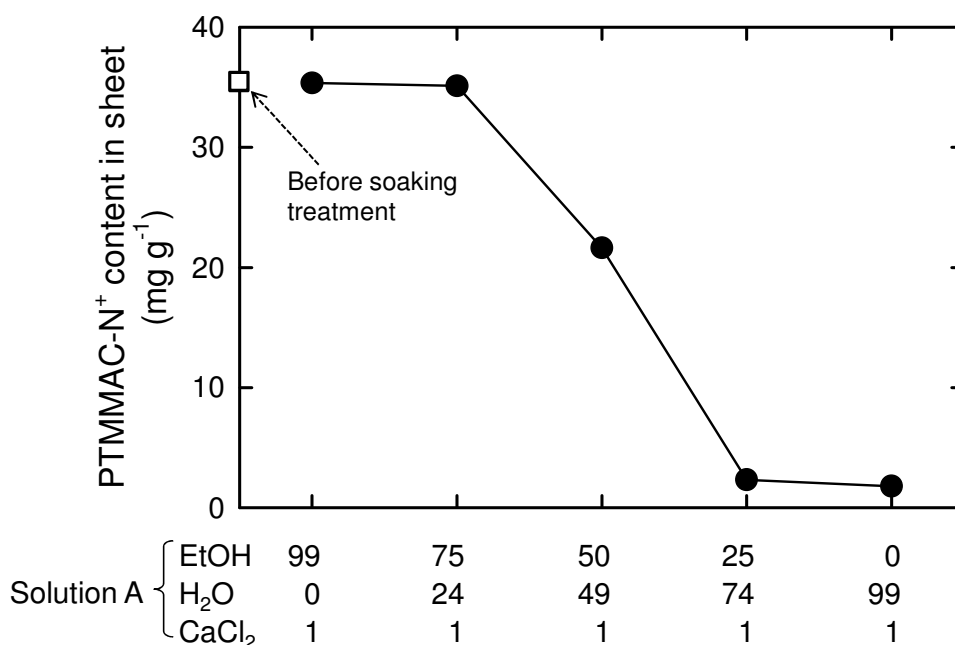
Figure 3.2 PTMMAC-N^+ content of the PTMMAC/CMC/cellulose sheets soaked in Solutions A with different weight ratios of the three components and then washed thoroughly with fresh EtOH to remove excess $CaCl_2$.

Calcium contents of the sheets soaked in Solutions A and then washed thoroughly with fresh EtOH to remove excess $CaCl_2$ were determined by XRFA, and depicted in Figure 3.3. In the case of the blank cellulose sheets prepared without PTMMAC or CMC, calcium contents corresponded well to the carboxyl content of the cellulose fiber (0.06 mmol g^{-1}), which were determined by the conductivity titration method (Table 3.1). This result indicates that $Ca^{2+}Cl^-$ ions were present as the counter ions of all carboxyl groups present in the blank cellulose sheets, forming the structure of cellulose-$COO^-Ca^{2+}Cl^-$ but not the cross-linked structures like (cellulose-$COO^-)_2Ca^{2+}$.
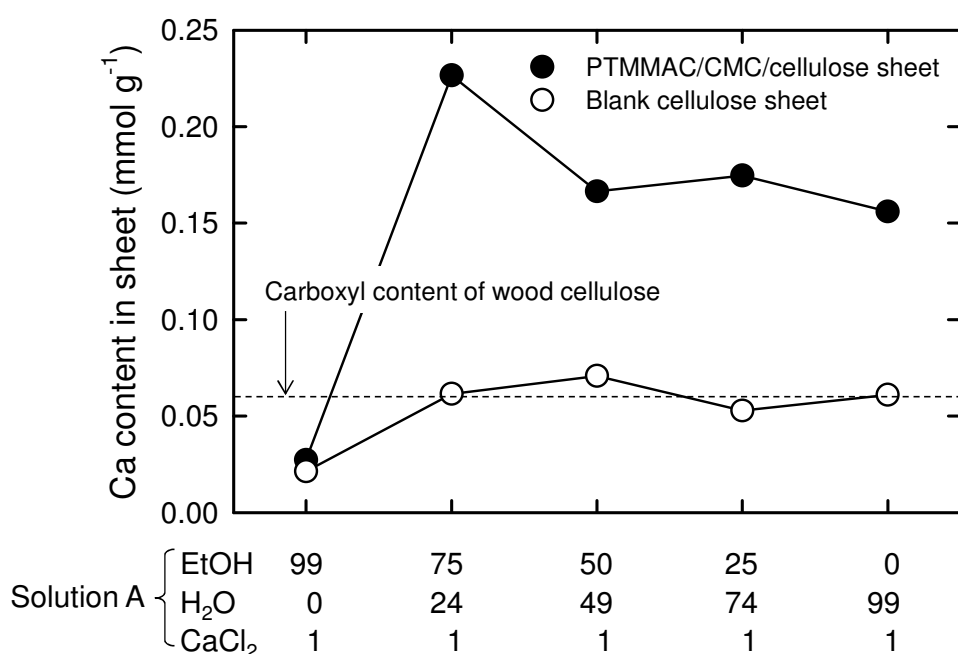
Figure 3.3 Calcium content of the PTMMAC/CMC/cellulose sheets soaked in Solutions A with different weight ratios of the three components and then washed thoroughly with fresh EtOH to remove excess $CaCl_2$.

When the PTMMAC/CMC/cellulose sheets were soaked in Solutions A, the highest calcium content of 0.23 mmol g^{-1} was observed, when the weight ratio of the soaking solution EtOH/H_2O/$CaCl_2$ was 75:24:1 (abbreviated hereafter to Solution A-75:24:1). The calcium contents decreased to approximately 0.16-0.17 mmol g^{-1}, when the soaking solutions with EtOH contents of 0-50% were used. In these cases, the PTMMAC/CMC/cellulose sheets were partly disintegrated to fibers during stirring in fresh EtOH after soaking in Solutions A so that a part of fine particles of PTMMAC/CMC polyion complexes may have been separated from the cellulose fiber

and lost during washing process by filtration. When Solution A-75:24:1 was used as the soaking solution, on the other hand, the sheet form was stably maintained in all cases examined. Based on the results in Figures 3.2 and 3.3, almost all PTMMAC and CMC molecules present in the original sheets remained in the sheets after soaking in Solution A-75:24:1.
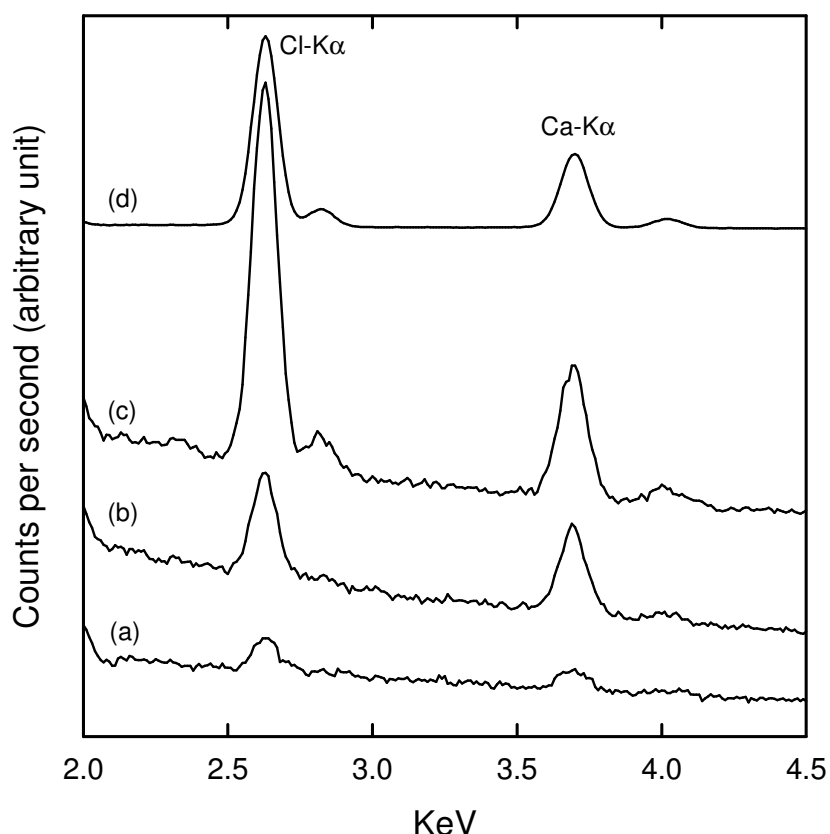
Figure 3.4 SEM-EDX spectra of the blank cellulose sheet soaked in Solution A-75:24:1. (a), the PTMMAC/CMC/cellulose sheets soaked in Solution A-25:74:1 (b) and Solution A-75:24:1 (c), and a mixture of $CaCl_2$ and microcrystalline cellulose powder (d).

Figure 3.4 displays SEM-EDX patterns of the blank cellulose sheet soaked in Solution A-75:24:1, the PTMMAC/CMC/cellulose sheets soaked in Solution A-25:74:1 and Solution A-75:24:1, and a $CaCl_2$/microcrystalline cellulose powder mixture. Quantitative analysis revealed that the blank cellulose sheet soaked in Solution A-75:24:1 and the PTMMAC/CMC/cellulose sheet soaked in solution A-25:74:1 had calcium and chlorine contents with almost 1:1 by mol. These results also support the hypothesis that calcium ions are present as the structures of cellulose-$COO^-Ca^{2+}Cl^-$ and CMC-$COO^-Ca^{2+}Cl^-$ in these sheets without forming the cross linkages of two

carboxylate groups by one Ca^{2+} ion. On the other hand, the PTMMAC/CMC/cellulose sheets soaked in Solution A-75:24:1 had calcium and chlorine contents with almost 1:2 by mol in a similar manner to that of the $CaCl_2$/cellulose powder mixture.

3.3.4 Structures of PTMMAC and CMC molecules in the sheets before and after soaking treatments

As shown in Figure 3.2, almost all PTMMAC-N^+ molecules remained in the sheets after soaking in Solution A-75:24:1. The structures of PTMMAC-N^+ and CMC-COO^- in the sheets before and after the soaking treatments are summarized and illustrated in Figure 3.5. Here, the interactions between carboxyl groups present in the original cellulose fiber and either PTMMAC molecules or Ca^{2+} ions are omitted, focusing on the interactions between PTMMAC-N^+, CMC-COO^- and Ca^{2+} ions. The most significant finding in this study is that carboxyl groups of CMC in the sheets do not form the cross linked structures of $(CMC\text{-}COO^-)_2Ca^{2+}$ or $(cellulose\text{-}COO^-)Ca^{2+}(^-OOC\text{-}CMC)$ but form the structures of CMC-$COO^-Ca^{2+}Cl^-$ and cellulose-$COO\text{-}Ca^{2+}Cl^-$ in the sheets after soaking in Solutions A with any weight ratios of $EtOH/H_2O/CaCl_2$.

The wet strength results in Figure 3.1 are well explainable by the structures of CMC molecules in Figure 3.5. When the PTMMAC/CMC/cellulose sheets are soaked in Solutions A containing EtOH and $CaCl_2$, the degrees of dissociation of carboxylate groups of the CMC-$COO^-Ca^{2+}Cl^-$ structures are sufficiently suppressed, resulting in appearance of wet tensile strengths of the soaked sheets to some extent. Meanwhile, all carboxylate groups of the CMC-$COO^-Ca^{2+}Cl^-$ structures can be dissociated in water, resulting in no wet strength associated by cleavage of most of inter-fiber bonds. If some cross-linked structures like $(CMC\text{-}COO^-)_2Ca^{2+}$ are present in the inter-fiber regions of the sheets, some wet strengths should appear on the sheets soaked in Solution A-0:99:1. [12), 14-16)]

Thus, the trade-off relationships of cellulose sheets between the appearance of wet strength in use and improvement of disintegrability in water after use can be achieved by the addition of CMC to cellulose sheets and the use of, for instance, Solution A-20:79:1 as the impregnation liquid of the sheet for wet wipers disposable in toilet water.

3.3.5 PTMMAC and CMC contents and their retention ratios in the sheets in sheet-making process

All PTMMAC and CMC molecules originally present in the PTMMAC/CMC/cellulose sheets were found to remain in the sheets after the soaking

treatment in Solution A-75:24:1, forming the left structure in Figure 3.5.
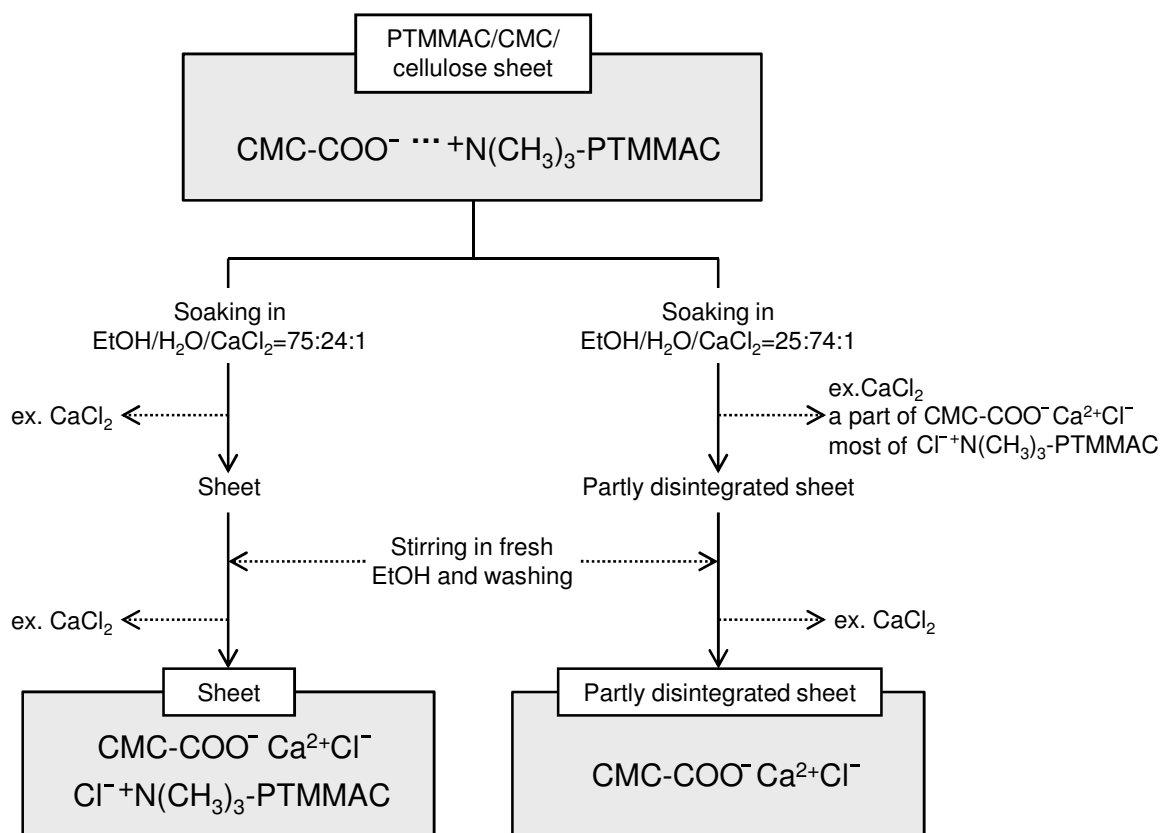
Figure 3.5 Schematic representation of chemical structures of PTMMAC and CMC components in the original PTMMAC/CMC/cellulose sheets and those after the soaking treatment in Solution A-75:24:1 or Solution A-25:74:1 followed by washing with fresh EtOH.

Thus, PTMMAC-N^+ and CMC-COO^- contents of the sheet before and after the soaking treatment in Solution A-75:24:1 were calculated from the PTMMAC-N^+ content (35.1 mg g^{-1}) in Figure 3.2 and calcium content (0.227 mmol g^{-1}) in Figure 3.3 (Details of calculation methods of PTMMAC-N^+ and CMC-COO^- contents of the sheet are described in Chapter 4). The results are listed in Table 3.2. When 5% PTMMAC-N^+Cl^- and 5% CMC-COONa (both percentages are based on the dry weight of the cellulose) were added in this order to the cellulose slurries, approximately 94% of both PTMMAC and CMC were retained in the cellulose sheets, forming carboxylate amine salts without any Ca^{2+} as counter ions of carboxyl groups of CMC molecules. Because the amount of surface carboxyl groups on the cellulose fiber was only 0.007

mmol g^{-1}, most of the PTMMAC and CMC molecules added to the cellulose slurries should be retained in the sheets as polyion complexes formed between PTMMAC and CMC molecules. Thus, more than 3% CMC contents in the cellulose sheets can be achieved using PTMMAC as the retention aid in papermaking process. Details of the retention mechanism of PTMMAC and CMC molecules in sheets during sheet-making process are reported in Chapter 5.

Table 3.2 PTMMAC, CMC and Ca^{2+} contents of the PTMMAC/CMC/cellulose sheets before and after the soaking treatment in Solution A with EtOH/H_2O/$CaCl_2$ weight ratio of 75:24:1.

Sample	PTMMAC-N$^+$ content (mg g^{-1})	CMC-COO$^-$ content (mg g^{-1})	Ca^{2+} content (mmol g^{-1})
Before soaking	35.8	39.3	0.000
(retention ratio, %)	(93.9)	(94.2)	–
After soaking	35.1	38.5	0.227

3.4 Conclusion

When the cellulose sheets were prepared from cellulose slurries with 5% PTMMAC and 5% CMC using a papermaking technique, approximately 94% of both PTMMAC and CMC, respectively, added were retained in the sheets, forming carboxylate amine salts between PTMMAC-N$^+$ and CMC-COO$^-$ molecules (and probably between PTMMAC-N$^+$ molecules and cellulose-COO$^-$ groups as well). When the PTMMAC/CMC/cellulose sheets were soaked in the solution of EtOH/H_2O/$CaCl_2$ with the weight ratio of 75:24:1, almost all PTMMAC and CMC molecules remained in the sheets, forming the structures of PTMMAC-N$^+$Cl$^-$ and CMC-COO$^-$Ca^{2+}Cl$^-$. Thus, accurate PTMMAC-N$^+$, CMC-COO$^-$ and Ca^{2+} contents in the soaked and then dried sheets could be calculated from nitrogen, calcium and chlorine contents determined by analytical methods. When the EtOH/H_2O/$CaCl_2$ solution with the weight ratio of 20:79:1 was used in the soaking treatment, sufficient wet tensile strength of 6 Nm g^{-1} appeared on the sheet, probably because of low dissociation degrees of carboxylate groups of the CMC-COO$^-$Ca^{2+}Cl$^-$ structures in the EtOH-containing soaking solutions. On the other hand, no wet strength was observed for the sheets soaked in the

EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 0:99:1 by sufficient dissociation of the CMC-COO$^-$Ca^{2+}Cl$^-$ structures in water. Thus, the conflicting properties of wet strength and water-disintegrability can be added to the PTMMAC/CMC/cellulose sheets by selecting weight ratios of EtOH/H$_2$O/CaCl$_2$ used as the impregnation liquid for wet wiping sheets. In Chapter 5, details of the retention mechanism of PTMMAC and CMC molecules in sheets during sheet-making process are reported.

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Chapter 4

Establishment of determination methods of polymer contents in cellulose sheets

4.1 Introduction

It is very important to know the accurate amounts of polymers retained in cellulose sheets prepared with these polymers and cellulose fibers, when the retention behavior of polymers and the physical properties of the cellulose sheets are analyzed in the following chapters. Cationic polymer contents containing amino groups or quaternary ammonium groups such as poly[*N*,*N*,*N*-trimethyl-*N*-(2-methacryloxylethyl)ammonium chloride] (PTMMAC) can be estimated easily from nitrogen contents determined by elementary analysis, using combustion-type gas-chromatography. [1] In the past, the Kjeldahl method that needs troublesome and time consuming procedure was popularly adopted. [2] However, in order to calculate cationic polymer contents in the cellulose sheet more accurately, another modified method is required.

On the other hand, determination of carboxymethyl cellulose (CMC) contents in the sheets prepared by the dual polymer system (abbreviated hereafter to DP-cellulose sheet) was difficult, because CMC was retained in the sheet with cationic polymer. If only CMC retains in the cellulose sheet, polyelectrolyte titration, electric conductivity titration, infrared resonance attenuated total reflectance spectroscopy (IR-ATR) or infrared reflection absorption spectroscopy (IRRAS) using polarized light are available for the determination of CMC in the sheet. [3,4] However, these methods are not available for the determination of CMC in DP-cellulose sheets. As to methods for determining CMC contents in DP-cellulose sheets, various methods had been proposed. One of the methods is: 1) extraction of CMC molecules from the samples with sodium hydroxide. 2) Treatment of the extracted CMC molecules with sulfuric acid to produce glycolic acid, and 3) colorimetric measurement of the glycolic acid. [5] Another method is phenol-sulfuric acid test. [6,7] However, complicated and time consuming procedures are required for these methods, which are not convenient for treating a lot of samples. Therefore, a new method is required for the estimation of CMC contents in DP-cellulose sheets. In Chapter 3, it was found that the CMC molecules retained in DP-cellulose sheets formed the CMC-COO$^-$Ca^{2+}Cl$^-$ structure after soaking the sheet in the solution consisting of ethanol, water, and calcium chloride (EtOH/H$_2$O/CaCl$_2$ solution). This result leaded to establishment of a new determination method of CMC

content in DP-cellulose sheets.

In this chapter, determination methods of carboxymethyl cellulose (CMC) and poly[*N,N,N*-trimethyl-*N*-(2-methacryloxylethyl)ammonium chloride] (PTMMAC) contents in cellulose sheets are described in detail in order to supplement some additional information.

4.2 Materials and methods

4.2.1 Materials

A commercial softwood bleached kraft pulp without beating (750 mL Canadian Standard Freeness) was used as the cellulose fiber in sheet-making. A sodium carboxymethyl cellulose (CMC; Daiich-Kokyo Seiyaku Co., Ltd., Japan) with DS 0.96 and DP_w value of 640, and poly[*N,N,N*-trimethyl-*N*-(2-methacryloxylethyl)ammonium chloride] (PTMMAC) with DP_w of 342 were used in sheet-making. The fundamental characteristics of CMC, PTMMAC, and cellulose fiber used here, measured by some methods described in Chapter 2, are listed in Table 3.1 (Chapter 3). One % (w v^{-1}) solutions of CMC and PTMMAC were prepared with distilled water, and used as additives in sheet-making process. Other chemicals and solvents were of laboratory grade (Wako Pure Chemicals Co., Japan) and used as received.

4.2.2 Cellulose sheet-making with PTMMAC and CMC

The cellulose fiber (10 g) was suspended in tap water (1 L) under continuous stirring at 300 rpm. The 1% PTMMAC solution (50 mL) was first added to the cellulose slurry. After stirring for 1 min, the 1% CMC solution (50 mL) was then added. Hence, the addition levels of PTMMAC and CMC were both 5% based on the dry weight of the cellulose. After additional stirring for 3 min, cellulose sheets with a basis weight of 60 g m^{-2} were prepared from the slurry with tap water according to the procedure described in Chapter 3. The cellulose sheets (DP-cellulose sheet) containing PTMMAC and CMC thus obtained were conditioned at 23 °C and 50% relative humidity for more than 1 day.

4.2.3 Analyses of basic data for the calculation of PTMMAC or CMC contents in cellulose sheets

In order to analyze the PTMMAC-N^+ contents of DP-cellulose sheets, it is important to determine the nitrogen contents of the sheets. The nitrogen contents of the sheets were determined by combustion-type gas-chromatography (FLASH EA1112 NC-analyzer; Thermo Fisher Scientific Inc, US). [1] The calculation procedure of PTMMAC-N^+ contents of the sheets is mentioned later.

In order to analyze the CMC contents of DP-cellulose sheets, calcium ions (Ca^{2+}) and chloride ions (Cl^-) contents of the sheets after the soaking treatment in the solution consisting of ethanol (EtOH), water (H_2O), and calcium chloride ($CaCl_2$) for at least 30 min and washing the sheets thoroughly in order to remove excess $CaCl_2$ in the sheets without disintegrating, were determined by X-ray fluorescence analyzer (XRFA) (MESA-500, Horiba, Japan) with X-ray generation at 15 kV and 500 μA according to a previously reported method. [8], [9] The reason why the soaking treatment time in the solution EtOH/H_2O/$CaCl_2$ was set up on at least 30 min, is that Ca content was saturated at least 15 min later after soaking the sheets in the solution EtOH/H_2O/$CaCl_2$, therefore, setting up the soaking time on at least 30 min in this experiment was valid in order to obtain appropriate data (Figure 4.1). The weight ratio of the soaking solution EtOH/H_2O/$CaCl_2$ was 75:24:1 (abbreviated hereafter to Solution A-75:24:1), because almost all PTMMAC and CMC remained in DP-cellulose sheets as PTMMAC-N^+Cl^- and CMC-$COO^-Ca^{2+}Cl^-$ without being removed from the sheets (Chapter 3).
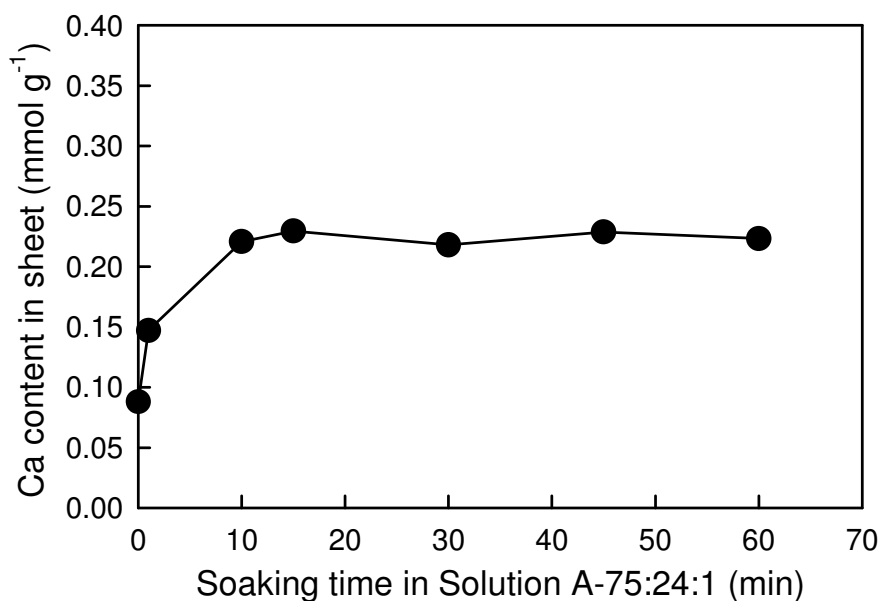

Figure 4.1 The effect of the soaking time in Solution A-75:24:1 on Ca content of PTMMAC/CMC/cellulose sheet.

4.2.4 Calculation of PTMMAC-N^+ content of DP-cellulose sheets

$$\text{PTMMAC-}N^+ \text{ content (mg g}^{-1}) = \frac{N}{14} \times 172 \times 10 \tag{1}$$

where N (%) is the nitrogen content of the sheet, and the value 172 is the molecular weight of one repeating unit of PTMMAC-N$^+$.

4.2.5 Calculation of CMC-COO$^-$ content of DP-cellulose sheets after soaking in EtOH/H$_2$O/CaCl$_2$ with the weight ratio of 75:24:1 followed by washing with fresh EtOH

According to Figures 3.2, 3.3 and 3.4, the PTMMAC and CMC molecules and carboxyl groups of cellulose after soaking in Solution A-75:24:1 have the structures of

PTMMAC-N$^+$ Cl$^-$
CMC-COO$^-$Ca^{2+}Cl$^-$
Cellulose-COO$^-$Ca^{2+}Cl$^-$

When 1 g cellulose with free carboxyl groups is used in sheet-making, the weight of cellulose-COOCaCl is 1.0047 g based on the carboxyl content 0.062 mmol g^{-1}. When the amounts of CMC-COO$^-$Ca^{2+}Cl$^-$ and PTMMAC-N$^+$Cl$^-$ to 1 g cellulose in the sheets are a g^{-1} and b g^{-1}, respectively,

$$\frac{b \times 172 \times 1000}{207.45 \times (1.0047 + a + b)} = \text{PTMMAC-N}^+ \text{ content (mg g}^{-1}) \qquad (2)$$

where the values of 172 and 207.45 are the molecular weights of one repeating unit of PTMMAC-N$^+$ and PTMMAC-N$^+$Cl$^-$, respectively.

$$\frac{0.062 + \dfrac{a}{289.55} \times 0.963 \times 1000}{1.0047 + a + b} = \text{calcium content (mmol g}^{-1}) \qquad (3)$$

where the value 0.062 is the carboxyl content (mmol g^{-1}) of the cellulose determined by the conductivity titration method, and the value 289.55 is the molecular weight of one repeating unit of CMC-COO$^-$Ca^{2+}Cl$^-$ with DS 0.963, which was calculated from carboxyl content of the CMC determined by the conductivity titration method (Table 3.1).

Therefore, if PTMMAC-N$^+$ and calcium contents after the soaking treatment in Solution A-75:24:1 are measured by above mentioned analyses (see 4.2.3), the values a and b can be obtained, and CMC-COO$^-$ content can be obtained by the following equation (4).

$$\frac{\dfrac{a}{289.55}\times 216.89\times 0.963\times 1000}{1.0047+a+b} = \text{CMC-COO}^{-} \text{ content (mg g}^{-1}) \qquad (4)$$

where the values 216.89 is the molecular weight of one repeating unit of CMC-COO⁻ with degree of substitution of 0.963.

4.3 Results and discussions

The values a and b can be obtained by solving the equations (2) and (3). Because PTMMAC-N⁺ and calcium contents in the PTMMAC/CMC/cellulose sheet after soaking in Solution A-75:24:1 are 35.12 mg g⁻¹ and 0.227 mmol g⁻¹, respectively, from Figures. 3.2 and 3.3 in Chapter 3, the values a and b are calculated to be 57.0 mg g⁻¹ and 47.0 mg g⁻¹, respectively.

Thus, the PTMMAC-N⁺ and CMC-COO⁻ contents in the sheet after soaking in Solution A-75:24:1 are calculated to be 35.12 mg g⁻¹ and 38.5 mg g⁻¹, respectively, from the chemical structures of the PTMMAC and CMC molecules in the sheet and the value (1.0047+a+b = 1.1087 g) of equation (3) (Table 4.1). Because no CaCl₂ is present in the sheet before the soaking treatment with Solution A-75:24:1, the PTMMAC-N⁺ and CMC-COO⁻ contents in the original PTMMAC/CMC/cellulose sheet are calculated to be 35.8 mg g⁻¹ and 39.3 mg g⁻¹, respectively, using the value of (1.1087-a×75.45×0.963/289.55-b×35.45/207.45=1.0864 g). When 5% PTMMAC-N⁺Cl⁻ and 5% CMC-COONa with DS 0.963 are added to the cellulose slurries, the amounts of PTMMAC-N⁺ and CMC-COO⁻ added are calculated to be 41.5 mg and 45.4 mg, respectively, to 1g cellulose. The retention ratios of PTMMAC-N⁺ and CMC-COO⁻ on the sheets are then calculated from b×172×100/41.5/207.45 and a×216.9×100/45.4/289.5, respectively, to be 93.9% and 94.27%, respectively (Table 4.1).

The determination method proposed in this chapter, is not only more convenient for treating a lot of samples but also safer for experimenters and environment than other methods, [2), 5), 6)] because a heated sulfuric acid with high concentration is not used and the quantity of waste liquid from experiments is little. However, this method is established based on the hypothesis that CMC retained in DP-cellulose sheets formed CMC-COO⁻Ca²⁺Cl⁻ structure after the soaking treatment in EtOH/H₂O/CaCl₂ solution from XRFA and SEM-EDX results (Chapter 3) and that calcium and chloride ions were homogeneously present in the sheets, which should be taken into consideration.

Table 4.1 PTMMAC, CMC and Ca^{2+} contents of the PTMMAC/CMC/cellulose sheets before and after the soaking treatment in Solution A with $EtOH/H_2O/CaCl_2$ weight ratio of 75:24:1.

Sample	PTMMAC-N$^+$ content (mg g^{-1})	CMC-COO$^-$ content (mg g^{-1})	Ca^{2+} content (mmol g^{-1})
Before soaking	35.8	39.3	0.000
(retention ratio, %)	(93.9)	(94.2)	–
After soaking	35.1	38.5	0.227

4.4 Conclusion

The simple determination methods of PTMMAC and CMC contents in cellulose sheets prepared with these polymers by the dual polymer system were established by calculation from nitrogen and calcium contents in the sheets, which were measured by elementary and X-ray fluorescence analyses, respectively. This determination method was not only accurate but also more convenient for measuring a lot of samples than other methods. However, this determination method is based on the assumption that elements such as calcium and chloride ions were homogeneously present in the sheets.

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Chapter 5

Retention behavior of polyion complexes formed between carboxymethyl cellulose and cationic polymer molecules in cellulose sheets for wet wiper

5.1 Introduction

In Chapter 3, carboxymethyl cellulose (CMC)-rich cellulose sheets were prepared by papermaking technique using a dual polymer system with poly[*N,N,N*-trimethyl-*N*-(2-methacryloxyethyl)ammonium chloride] (PTMMAC, Figure 2.1 in Chapter 2) as cationic polymer. PTMMAC/CMC/cellulose sheets were prepared with 5% PTMMAC and 5% CMC, and chemical structures of these additives in the sheets were analyzed. When the PTMMAC/CMC/cellulose sheets were soaked in solutions consisting of ethanol, water and calcium chloride (EtOH/H_2O/$CaCl_2$) with a weight ratio of 75:24:1, almost all PTMMAC and CMC molecules in the sheets turned to PTMMAC-N^+Cl^- and CMC-$COO^-Ca^{2+}Cl^-$ structures without dissolution into the soaking solution. Thus, PTMMAC, CMC and calcium contents in the sheets could be determined on the basis of these PTMMAC and CMC structures from analytical data such as nitrogen, calcium and chlorine contents.

In this Chapter, retention behavior of PTMMAC and CMC in cellulose sheets is studied in detail in terms of PTMMAC addition level, molecular weight of PTMMAC and surface charges of cellulose fibers and colloidal particles in PTMMAC/CMC/cellulose slurries using some analytical methods. Moreover, the effect of molecular weight of PTMMAC on dry and weight strengths, and water-disintegrability of the PTMMAC/CMC/cellulose sheets which are base materials for wet wiper sheets are investigated.

5.2 Materials and Methods

5.2.1 Materials

See Table 2.1 in Chapter 2 about the characteristics of cellulose fiber, CMC with DS 0.96, and PTMMACs with various DP_w values, which were used in this chapter. PTMMAC samples with various DP_w values, synthesized according to the procedure described in Chapter 2 were used.

5.2.2 Sheet-making

Designed amounts of PTMMAC and CMC solutions were added in this order to a 1% cellulose slurry under continuous stirring at 300 rpm. The lapse of time between the PTMMAC and CMC additions was set to be 1 min. In a separate case, PTMMAC and CMC were first added in this order to water followed by addition of the wet cellulose. Cellulose sheets with a basis weight of 60 g m^{-2} were prepared from the cellulose slurry with tap water at pH 7.3 and 0.25 mS cm^{-1}, according to TAPPI T 205 sp-95 (2005). The wet-pressed webs were dried at 100°C for 2 min using a rotary drum-dryer. The cellulose sheets thus prepared were conditioned at 23°C and 50% relative humidity for more than one day.

5.2.3 General analyses

The water-disintegrabilities of the sheets were evaluated according to a Japan Industrial Standard Testing method (JIS) P4501 (1993). A square-cut sheet with 60×60 mm was subjective to the soaking treatment in mixtures (100mL) of EtOH, H_2O, and $CaCl_2$ for 30 min. The weight ratio of the mixtures $EtOH/H_2O/CaCl_2$ was 25:74:1. Water (300 mL) in a beaker was first stirred at 600 rpm with a disk-type magnetic stirrer bar 35 and 12 mm in diameter and thickness, respectively. As the magnetic stirrer instrument, HI 304N (HANNA Instruments Co., USA) was used. When the square-cut sheet with 60×60 mm after the soaking treatment was dropped in the stirred water, the stirring speed initially decreased below 500 rpm due to the resistance of the dropped sheet and then increased as the disintegration of the sheet proceeded in water. The time required for recovering the stirring speed to 540 rpm was measured 5 times for each sample, and the average value was defined as "time required for dispersion of the sheet to fibers in water." The procedure of the water-disintegrability testing method of the sheets is shown in Figure. 5.1.

Details of the following analyses were described in the previous Chapters: ionic charge densities of CMC and PTMMAC (Chapter 2), DP_w values of PTMMACs (Chapter 2), dry tensile strength of cellulose sheets, wet tensile strength of cellulose sheets after soaking in mixtures of $EtOH/H_2O/CaCl_2$ with various weight ratios (Chapter 3), and PTMMAC-N$^+$ and CMC-COO$^-$ contents in the sheets (Chapters 3 and 4). The distribution of calcium of cellulose sheets were evaluated using mapping mode of an energy-dispersive X-ray (EDX) spectroscope in quantitative mode (EMAX-5770X; Horiba, Japan) attached with a scanning electron microscope (SEM) (S-4000; Hitachi High-Technologies Corp., Japan) at 20 μA for 4000 s after osmium coating with OsO4 gas at 10 mA for 10 s (Neoc, Meiwafosis Co., Ltd., Japan).
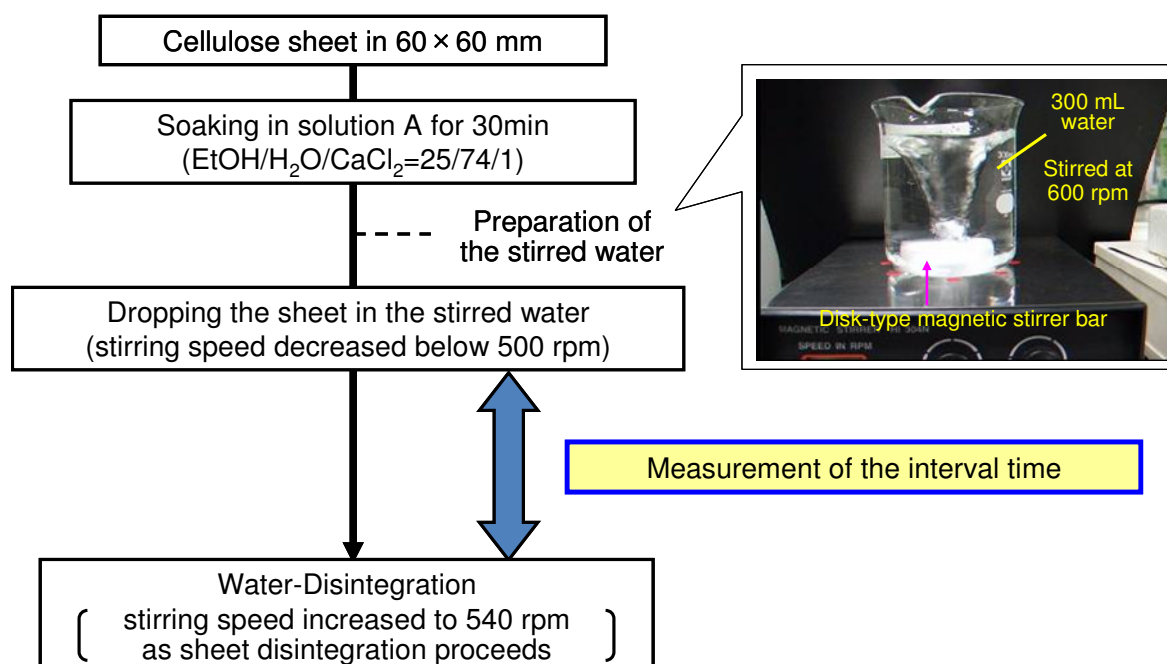
Figure 5.1 Procedure of the water-disintegrability testing method of cellulose sheets.

5.2.4 Characterization of cellulose fibers and colloidal particles in PTMMAC/CMC/cellulose slurries

The cellulose fiber (1.2 g) was stirred in 0.002M $NaNO_3$ (120 mL), which had the same pH and conductivity values as those of the tap water used in sheet-making. 1-7 % PTMMAC and 5% CMC (both percentages were based on dry weight of the cellulose) were added in this order to the cellulose slurry. After being stirred for 3 min, the cellulose slurry was filtered in a glass funnel (P-40 with pore size of 16-40 μm) by suction. The filtrate was diluted to 200 mL with 0.002M $NaNO_3$, and then subjected to measurements of UV-vis light transmittance and ζ-potential/z-average particle size at 25°C using a Shimadzu UV-1700 and a Malvern Zetasizer 3000, respectively. Further, the cellulose fiber mat formed on the glass funnel was washed thoroughly with 0.002M $NaNO_3$ by filtration, and then the cellulose fiber mat was dispersed to fibers in 0.002M $NaNO_3$ (500 mL). Zeta potentials of the cellulose fibers were measured at 25 °C by streaming potential method using a System Zeta Potential SZP04 (BTG Mütek GmbH, Germany). [1)]

5.3 Results and discussions

5.3.1 Retention of PTMMAC in sheet

Figure 5.2 shows the effect of PTMMAC addition level to cellulose slurries on the PTMMAC-N^+ content in the sheets and the corresponding retention ratio. The lapse of

time between the PTMMAC addition and sheet-making was set to be 1 min. The PTMMAC with DP_w of either 342 or 6450 was used as a sole additive to cellulose slurries. Similar retention patterns were obtained for the two cationic polymers. However, the maximum and plateau PTMMAC-N^+ contents in the sheets at 1-5% addition levels were different to some extent; approximately 1.7 and 1.4 mg g^{-1} for the sheets prepared with the polymers having DP_w of 342 and 6450, respectively. It is well known that higher amounts of cationic polymers with lower molecular weights adsorb on negatively charged cellulose fibers in water, because such polymers can penetrate also into small pores present on cellulose fiber surfaces to be fixed there by electrostatic interactions. [2-5]
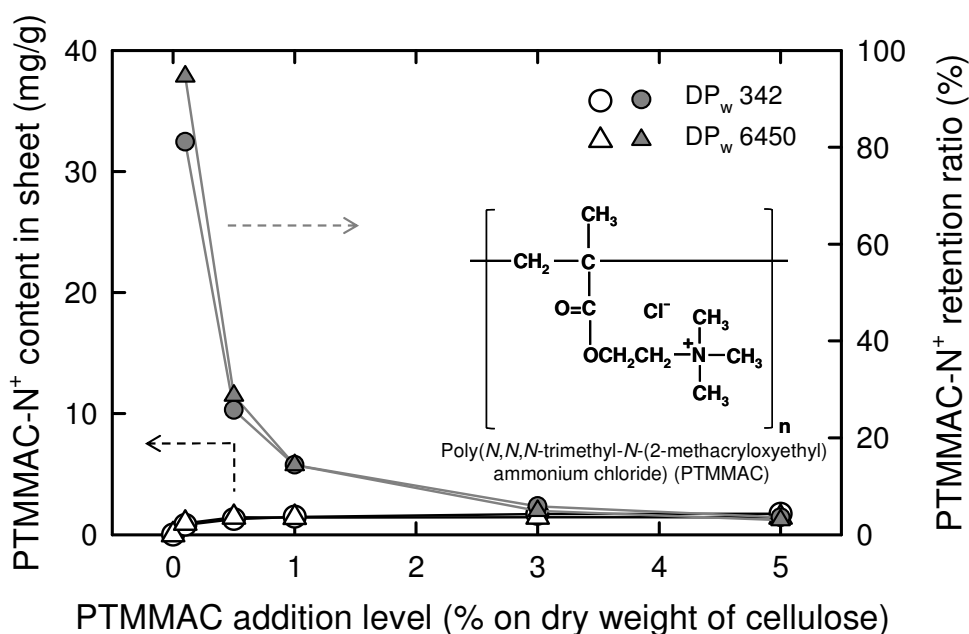
Figure 5.2 PTMMAC-N^+ content and the corresponding PTMMAC-N^+ retention ratio in sheets prepared with 0-5% PTMMAC.

However, the retention ratios were lower than 15% at 1-5% addition levels for both PTMMACs, showing that more than 85% of the added PTMMAC-N^+ electrolytes were present in the drainage water without adsorption on cellulose fibers during the sheet-making process. Thus, there were explicit limitations of the amount of PTMMAC-N^+ retained in the sheets, when only PTMMAC is added to cellulose slurries.

5.3.2 Retention behavior of PTMMAC and CMC in sheets prepared by dual polymer system

The amounts of PTMMAC-N$^+$ retained in the sheets significantly increased by the dual system using CMC as the co-additive, regardless of the DP$_w$ values of PTMMACs (Figure 5.3). When 5% PTMMAC and 5% CMC were added in this order to cellulose slurries, the PTMMAC-N$^+$ contents in the sheets reached approximately 30 mg g^{-1} for both PTMMACs with different DP$_w$ values, which corresponded to ~80% retention ratios. In contrast, when the addition levels of PTMMACs were 1, 3 and 7%, the PTMMAC-N$^+$ contents or the retention ratios were lower than those obtained for the sheets prepared with 5% PTMMAC and 5% CMC. The low PTMMAC-N$^+$ retentions were caused by imbalanced charges between cationic and anionic groups in the cellulose slurries, as described later.

Figure 5.3 PTMMAC-N$^+$ content and the corresponding PTMMAC-N$^+$ retention ratio in sheets prepared by dual polymer system with 1-7% PTMMAC and 5% CMC.

The CMC-COO$^-$ content in the sheets or the corresponding retention ratio versus the PTMMAC addition level are depicted in Figure 5.4. The patterns were similar to those for the PTMMAC-N$^+$ contents in Figure 5.3; the highest CMC-COO$^-$ contents/retentions were achieved at the 5% PTMMAC addition level, in which the retention ratios of CMC-COO$^-$ reached ~90%. The difference in DP$_w$ of PTMMACs had almost no influence on the CMC-COO$^-$ retention. Thus, the cellulose sheets containing

considerable amounts of CMC-COO$^-$ electrolytes, i.e. 35~38 mg g^{-1}, can be prepared by the dual polymer system using cationic PTMMAC as the co-additive.

The maximum amounts of PTMMAC-N$^+$ retained in the sheets were only 1.4-1.7 mg g^{-1}, when only PTMMAC was added to the cellulose slurries (Figure 5.2). Hence, the high PTMMAC-N$^+$ and CMC-COO$^-$ contents in the sheets were supposed to be achieved by forming polyion complexes between the cationic and anionic polymers in the cellulose slurries. In these cases, the charge balance between cationic PTMMAC-N$^+$, anionic CMC-COO$^-$ and anionic cellulose fibers must be the primary factor influencing the surface charges of cellulose fibers and polyion complexes formed in situ, which might result in the different retentions of the additives in Figures 5.3 and 5.4.
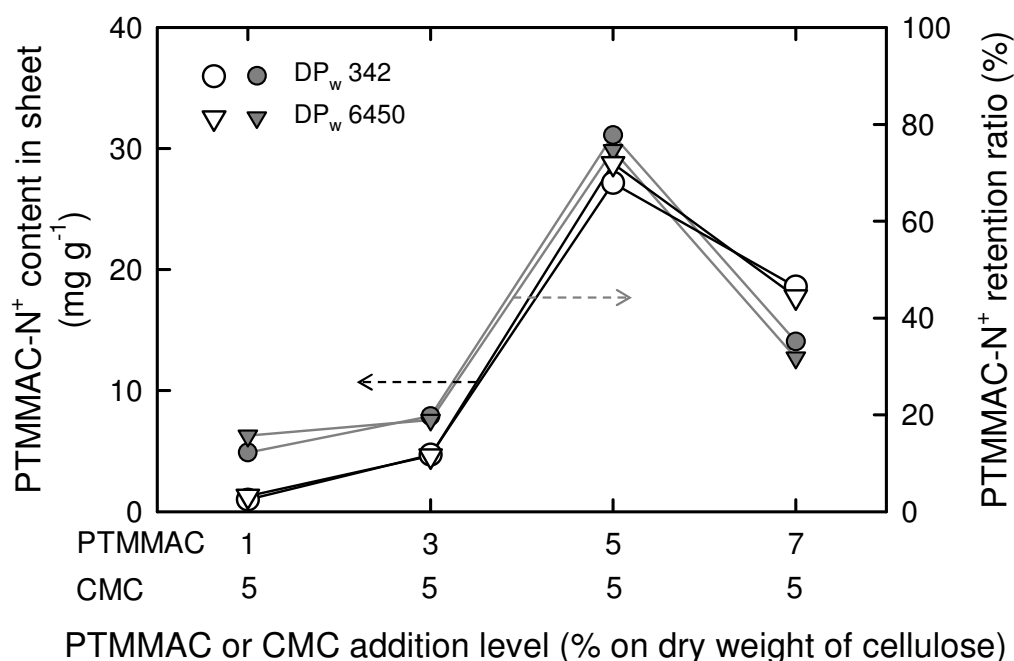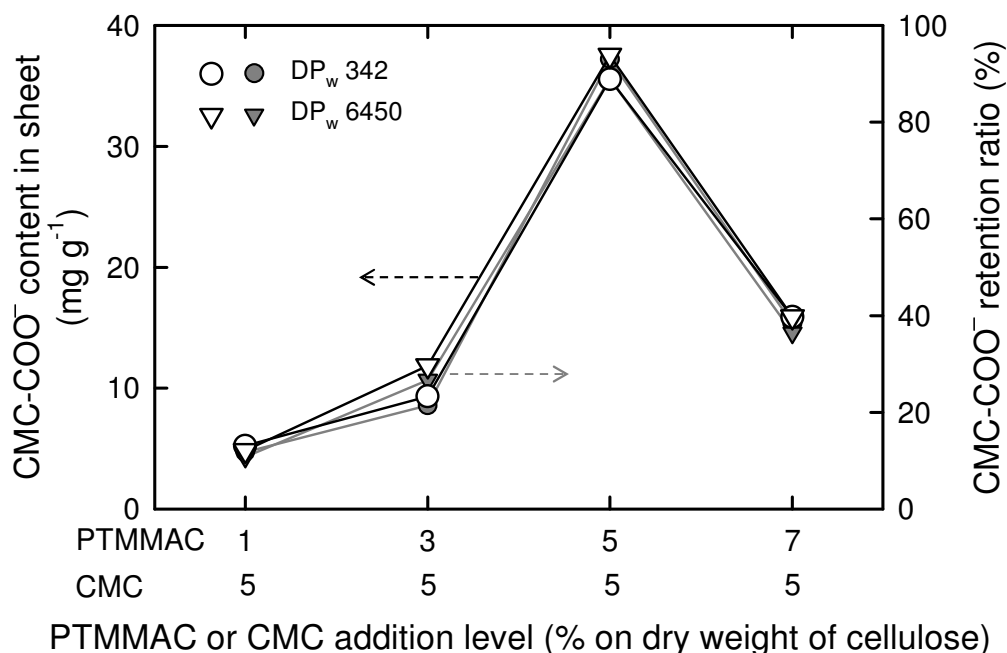

Figure 5.4 CMC-COO$^-$ content and the corresponding CMC-COO$^-$ retention ratio in sheets prepared by dual polymer system with 1-7% PTMMAC and 5% CMC.

Figure 5.5 shows ζ-potentials of cellulose fibers and colloidal particles in the cellulose slurries, which were prepared with 1-7% PTMMAC and 5% CMC. As expected, both cellulose fibers and colloidal particles had ζ-potentials close to zero, when 5% PTMMAC and 5% CMC were added, which consequently brought about the highest retentions of PTMMAC-N$^+$ and CMC-COO$^-$ electrolytes. [6]

Both cellulose fibers and colloidal particles had positive surface charges at the 6-7%

PTMMAC addition level. Electrostatic repulsion might act between cellulose fibers and colloidal particles or between colloidal particles themselves, resulting in lower retentions of both PTMMAC-N$^+$ and CMC-COO$^-$ electrolytes. Contrastively, both cellulose fibers and colloidal particles had negative surface charges at the 1-4.3% PTMMAC addition levels, resulting also in lower retentions of both electrolytes.
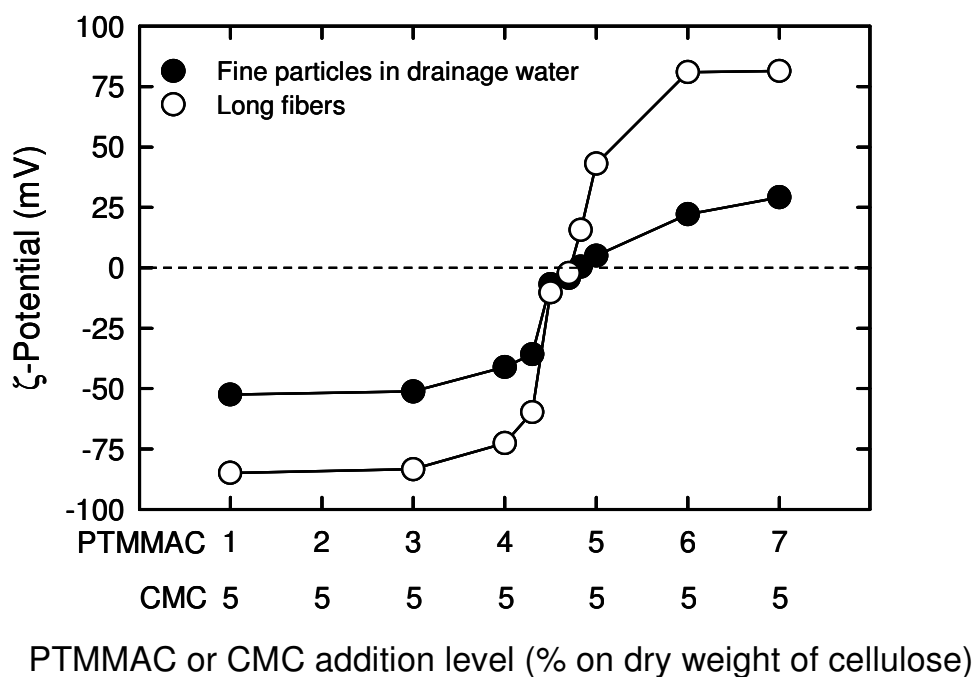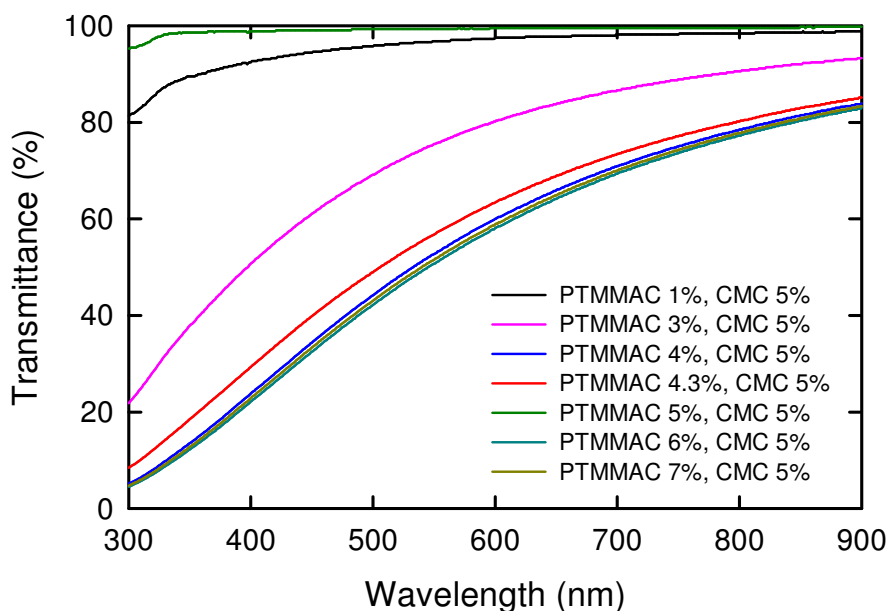

Figure 5.5 ζ-Potentials of cellulose fibers and colloidal particles in cellulose slurries. 1-7% PTMMAC with DP$_w$ 342 and 5% CMC were added to cellulose slurries.

  UV-vis light transmittances of the filtrates and the corresponding optical photos are presented in Figure 5.6. Expectedly, the light transmittance of the filtrate was the highest for the cellulose slurry prepared with 5% PTMMAC and 5% CMC, because almost all PTMMAC and CMC electrolytes adsorbed on cellulose fibers, forming polyion complexes. In contrast, the colloidal particles of PTMMAC/CMC polyion complexes were stably present in the filtrates by electrostatic repulsions at other PTMMAC addition levels. The PTMMAC/CMC colloidal particles formed in the cellulose slurry were quite small in quantity at the 1% PTMMAC addition level, resulting in such a high UV-vis light transmittance in Figure 5.6. Thus, the retention behavior of PTMMAC-N$^+$ and CMC-COO$^-$ electrolytes observed in Figures 5.3 and 5.4 is interpretable by charge balance between anionic and cationic groups present in the cellulose slurries. [6] In conclusion, such large amounts of anionic CMC-COO$^-$ electrolytes can be retained in cellulose sheets by the dual polymer system used in this

study. Retention behaviors of PTMMAC and CMC in sheets prepared by dual polymer system mentioned above are illustrated in Figure 5.7 in terms of charge balance between anionic and cationic groups present in the cellulose slurries.

Addition of PTMMAC (%)	1	3	4	4.3	5	6	7
Transmittance at λ=600nm (%)	97.5	80.2	60.0	63.4	99.5	58.1	58.9

Figure 5.6 UV-vis light transmittances and the corresponding photos of filtrates of cellulose slurries. 1-7% PTMMAC with DP_w 342 and 5% CMC were added to cellulose slurries.
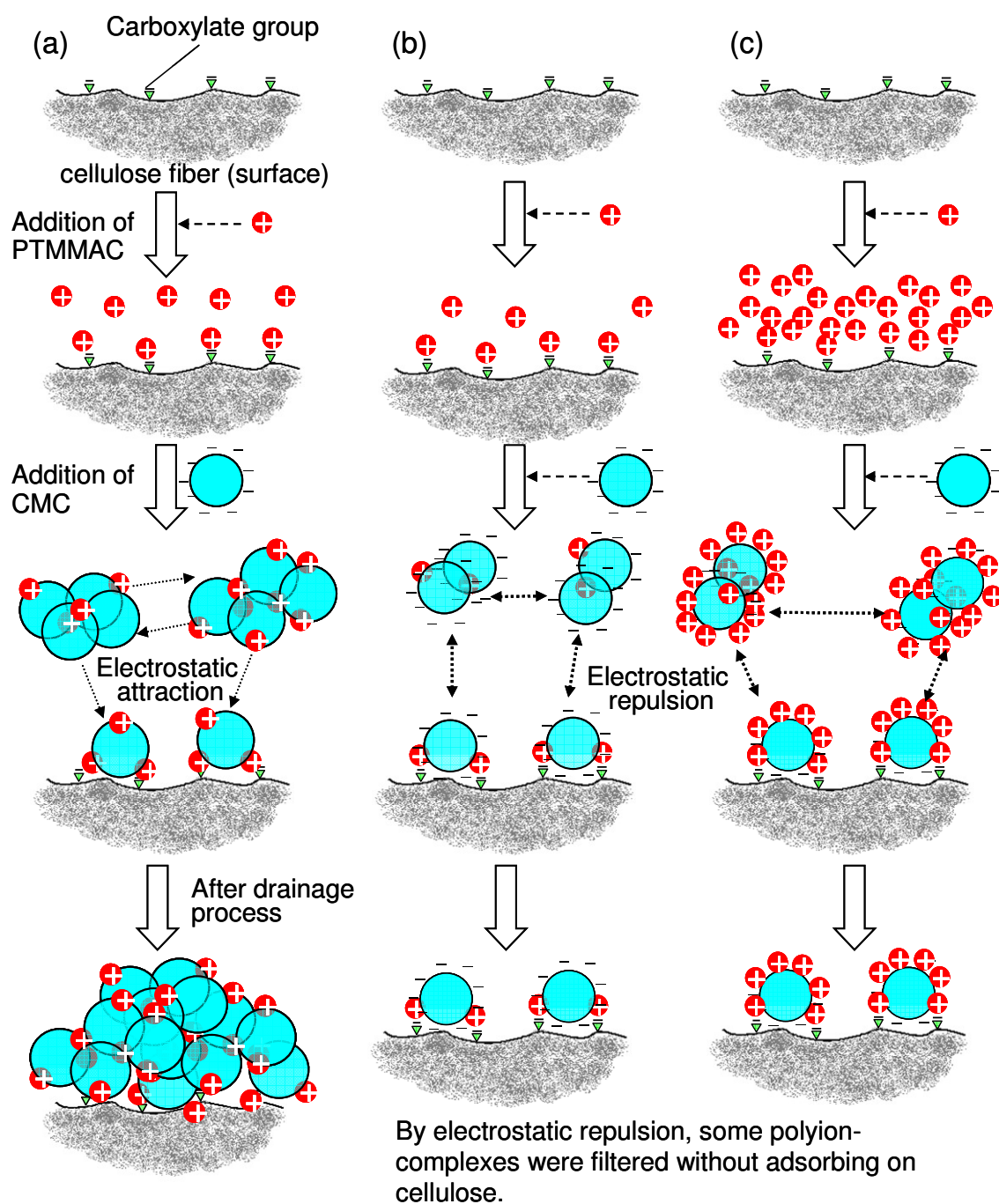
Figure 5.7 The mechanism of the polyion-complex's adsorption on cellulose fiber when PTMMAC's addition level was changed and CMC's addition level was fixed to 5% on dry weight of cellulose fiber. (a) The addition level of PTMMAC was 5% on dry weight of cellulose, (b) The addition level of PTMMAC was 1-4%, and (c) The addition level of PTMMAC was 6-7%. In this figure, the sizes of PTMMAC with DP_w of 342 and CMC are based on Radii of gyration determined by SEC-MALLS (Table 2.1 in Chapter 2).

5.3.3 Effects of addition level and DP$_w$ of PTMMAC on dry strength of the sheets

One of the properties required for wet wiper sheets made of cellulose fibers is to have sufficient wet tensile strengths in use. Dry tensile strengths of more than 40 Nm g^{-1} are also needed for the sheets in manufacturing and embossing processes without web-break. Moreover, there is a clear link between wet and dry strengths of the PTMMAC/CMC/cellulose sheets; the higher the dry strength of the sheets, the higher the wet strength as well. Thus, dry tensile strength of the PTMMAC/CMC/cellulose sheets provides an indication of the wet strength properties required for wet wiper sheets.
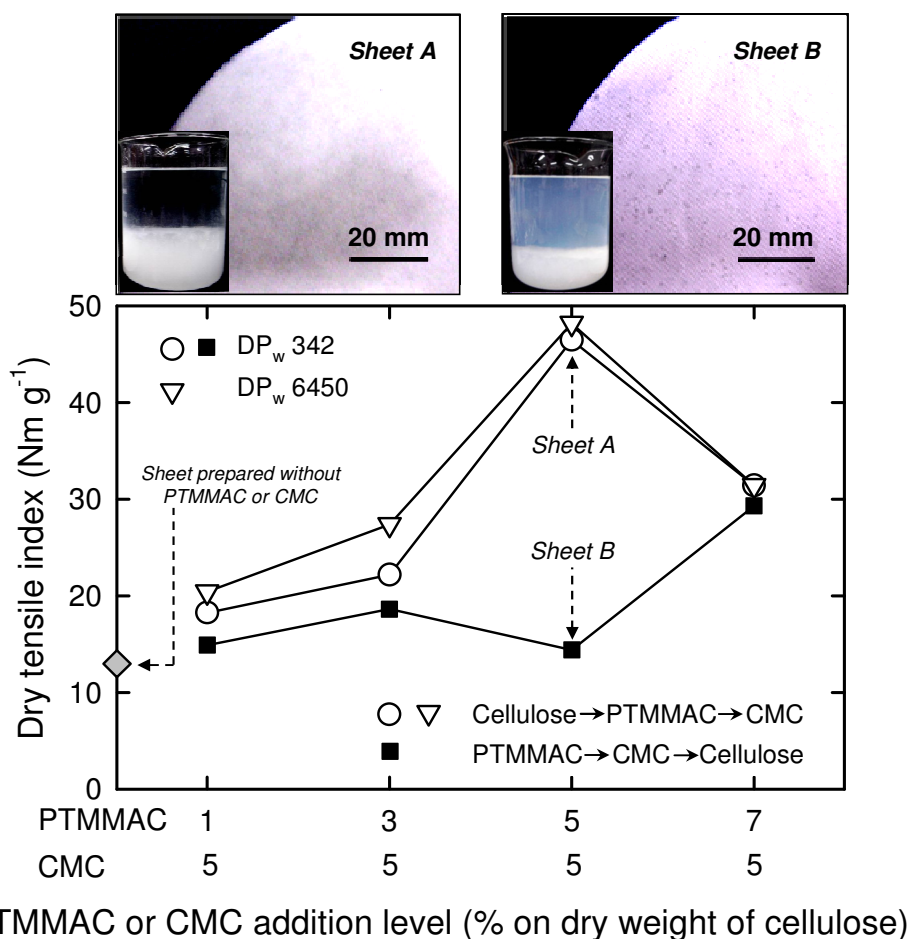

Figure 5.8 Dry tensile strength of sheets prepared with 1-7% PTMMAC and 5% CMC. The effects of addition order of additives on dry tensile strength and appearance of the cellulose slurries and dried sheets are presented also in this figure.

Dry tensile strengths of the sheets prepared with 1-7% PTMMAC and 5% CMC are

depicted in Figure 5.8. The highest dry-tensile strengths were expectedly observed for the sheets prepared with 5% PTMMAC and 5% CMC. The levels of such dry tensile strength were comparable to those prepared from beaten cellulose fiber of 400-500 mL Canadian Standard Freeness without any additives. Hence, the PTMMAC and CMC electrolytes retained as polyion complexes in the sheets play a role in improving inter-fiber bonds. Because the cellulose sheets prepared with the PTMMAC with DP_w of 6450 had slightly higher dry tensile strengths at 1, 3 and 5% PTMMAC addition levels than those prepared with PTMMAC with DP_w of 342, PTMMAC molecules with higher DP_w may have some contribution to higher dry tensile strengths of the sheets.
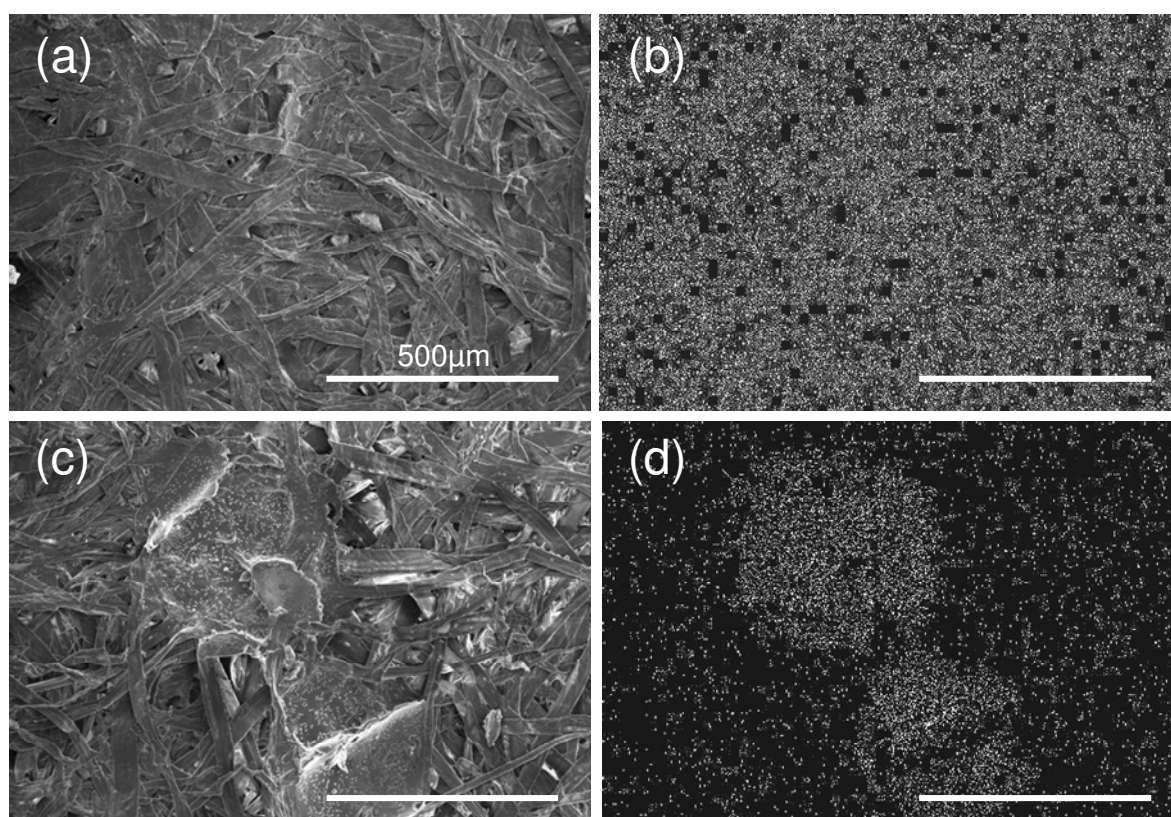
Figure 5.9 SEM images of Sheet A (prepared in the normal addition sequence, i.e. cellulose→PTMMAC→CMC) and Sheet B (prepared by the PTMMAC→CMC→ cellulose addition sequence), and Ca mapping images of these sheets by SEM-EDX after the soaking treatment in EtOH/H_2O/$CaCl_2$ solution with weight ratio of 75:24:1. (a) SEM image of Sheet A, (b) Ca mapping image of Sheet A, (c) SEM image of Sheet B, and (d) Ca mapping of Sheet B.

When the cellulose slurry was prepared by the different addition sequence, in which

PTMMAC and CMC were first added to water followed by the addition of cellulose, dry tensile strength of the sheets (Sheet B in Figure 5.8) thus prepared was remarkably low particularly at the 5% PTMMAC and 5% CMC addition levels. The supernatant of the cellulose slurry prepared by the normal PTMMAC/CMC addition sequence was transparent, and the corresponding sheet surface (Sheet A in Figure 5.8) was smooth and had no visible particles from relatively macroscopic view. On the contrary, the supernatant of the cellulose slurry prepared by the PTMMAC→CMC→cellulose sequence was turbid, and many and large particles due to PTMMAC/CMC polyion complexes easily visible to the naked eye were present on the sheet surface (Sheet B in Figure 5.8). SEM images of Sheets A and B, and Ca mapping images of these sheets by SEM-EDX after the soaking treatment in EtOH/H_2O/$CaCl_2$ solution with weight ratio of 75:24:1 are shown in Figure 5.9. From the local view, Sheet A surface was also smooth and PTMMAC/CMC polyion complexes may have been retained uniformly in sheet A, because the distribution of Ca ions interacting with CMC in Sheet A was uniform (Figure 5.9 (b)). Thus, in the normal addition sequence, i.e. cellulose→PTMMAC→ CMC, the PTMMAC/CMC polyion complexes with smaller particle sizes are likely to form in the cellulose slurries, and mostly and homogeneously adsorb on cellulose fiber surfaces during the sheet-making process, resulting in high dry tensile strengths. Contrastively, when the PTMMAC and CMC were first added to water, large particles of polyion complexes were first formed in water, and these particles were then trapped heterogeneously on the sheets by filtration effect during the sheet-making process, resulting in low tensile strengths (Sheet B in Figure 5.8, Figure 5.9 (c) and (d)).

5.3.4 Wet strength and water-disintegrability of the sheets

It was found that wet strengths of the PTMMAC/CMC/cellulose sheets were improved by soaking the sheets in EtOH/H_2O/$CaCl_2$ solutions (Solutions A) with suitable weight ratios of the three components in Chapter 3. The influence of DP_w of PTMMACs on wet strength of the sheets soaked in Solutions A are displayed in Figure 5.10. No clear difference in wet strength patterns were observed between the two PTMMACs; the wet strength of the sheets decreased with increasing the weight ratio of water in Solutions A at the soaking treatment regardless of the DP_w values of PTMMACs. When 20-40% EtOH and 1% $CaCl_2$ were present in the soaking solutions, wet strengths of the sheets became more than 5 Nm g^{-1}, the level of which is sufficient for wet wiper sheets. Such Solutions A-containing water-based detergents may be used as impregnation solutions into the PTMMAC/CMC/cellulose sheets for wet wipers. The detailed mechanism to improve wet strength of the sheets by soaking in such Solutions A-containing EtOH and

CaCl$_2$ has been reported in Chapter 3.
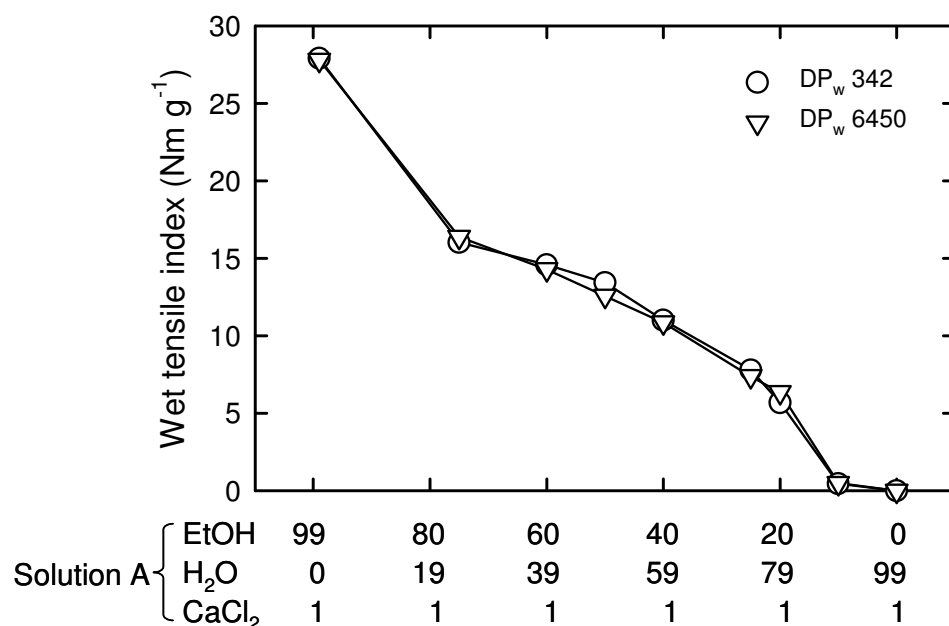
Figure 5.10 Wet tensile strength of sheets prepared with 5% PTMMAC and 5% CMC, after soaking in Solution A. PTMMACs with two different DP$_w$ values were used in sheet-making.

Figure 5.11 The sheet disintegration time (time required for dispersion of sheets to fibers by stirring in water) and PTMMAC content (residue) of the sh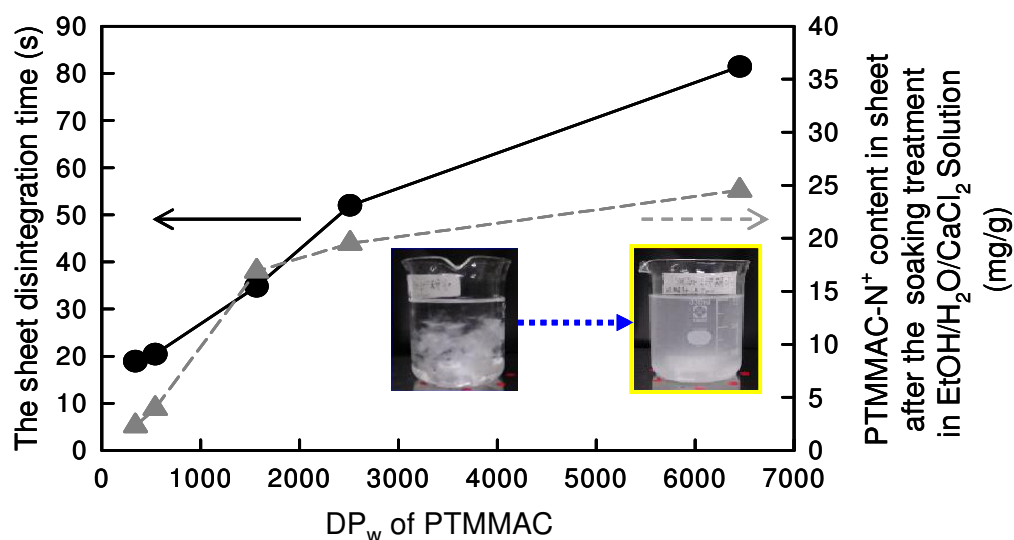eets. The sheets were prepared with 5% PTMMAC and 5% CMC. PTMMACs with different DP$_w$ values were used in sheet-making. The water-disintegrability of the sheets were evaluated after the soaking treatment in EtOH/H$_2$O/CaCl$_2$ solution with weight ratio of 25:74:1.

The CMC-COO$^-$ electrolytes present in the sheets forming polyion complexes with PTMMAC-N$^+$ electrolytes were found to be mostly turned to CMC-COO$^-$Ca^{2+}Cl$^-$ type-salt structures by exchanging the PTMMAC-N$^+$ electrolytes for CaCl$^+$ ions during the soaking treatment in Solutions A containing EtOH and CaCl$_2$. Degrees of dissociation of such CMC salts are restricted to some extent in the soaking solutions containing EtOH, resulting in wet strength development. When the sheets impregnated with Solution A containing EtOH and CaCl$_2$ are soaked in 100% water, the sheets are in turn disintegrable because degrees of dissociation of the CMC-COO$^-$Ca^{2+}Cl$^-$ salts are enhanced in water. Thus, sufficient wet strengths are allowed to appear on the sheets impregnated with Solution A in use but the sheets have sufficient disintegrability in toilet water after use.
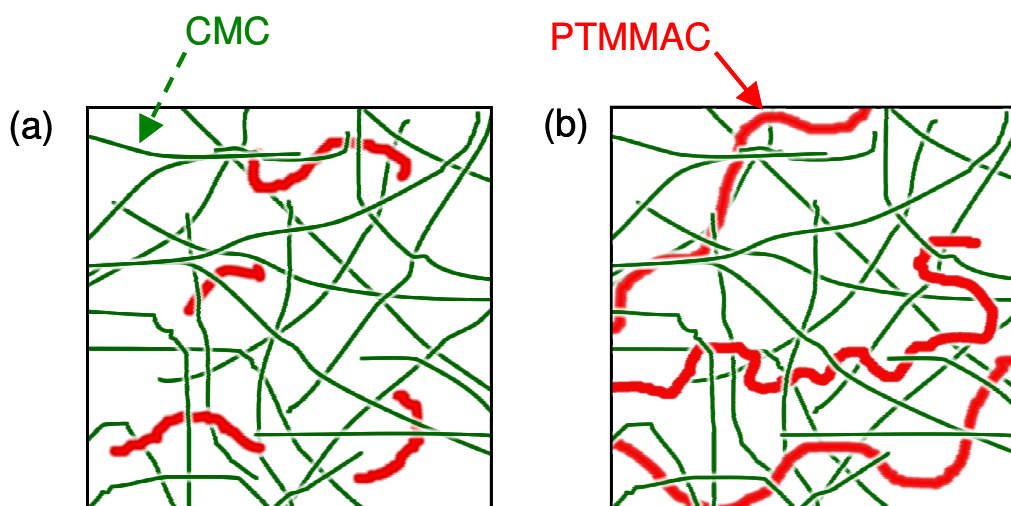
Figure 5.12 The illustrations of the interactions between CMC-COO$^-$Ca^{2+}Cl$^-$ matrix and PTMMAC-N$^+$Cl$^-$ chains. (a) The interactions between CMC matrix and short PTMMAC chains (with lower DP$_w$). There are small number of entanglement points between PTMMAC chains with lower DP$_w$ and CMC matrix. (b) The interactions between CMC matrix and long PTMMAC chains (with higher DP$_w$). There are large number of entanglement points between PTMMAC chains with higher DP$_w$ and CMC matrix.

Figure 5.11 shows the relationship between DP$_w$ of PTMMAC and the time required for disintegration of the PTMMAC/CMC/cellulose sheets to fibers in water by stirring. The disintegrability of the sheets in water sharply decreased or the time required for disintegration of the sheets drastically increased, when the PTMMAC with DP$_w$ of more than 1500 was used in the sheet-making. Thus, the PTMMACs with low DP$_w$ of ~340 are better to be used in sheet-making for the PTMMAC/CMC/cellulose sheets having

sufficient water-disintegrability after use. The water-disintegrability of the sheets can be related to the PTMMAC residue in the sheets after the soaking treatment in the EtOH/H_2O/$CaCl_2$ solution with weight ratio of 25:74:1. As shown in Figure 5.11 or Chapter 3, almost all the PTMMAC with DP_w of 342 was removed from the sheets as the PTMMAC-N^+Cl^- after the soaking treatment, however, the PTMMAC-N^+Cl^-s with higher DP_w of more than 1500 retained in the sheets was hard to be removed from the sheets after similar treatment. Therefore, PTMMAC molecules with higher DP_w of more than 1500 remaining in the sheets after the soaking treatment may be entangled complicatedly with CMC-$COO^-Ca^{2+}Cl^-$ matrix in the sheets, and such entanglement may prevent the bonds between CMC-$COO^-Ca^{2+}Cl^-$ molecular chains (CMC-$COO^-Ca^{2+}Cl^-$ matrix) from being broken in stirred water, resulting in the lower water-disintegrability of the sheets (Figure 5.12). [7]

5.4 Conclusions

Relatively large amounts of CMC molecules can be retained in the cellulose sheets, when PTMMAC is used as the co-additive in the cationic/anionic dual polymer system. When 5% PTMMAC and 5% CMC are added to the cellulose fiber slurry, PTMMAC-N^+ and CMC-COO^- of ~30 mg g^{-1} and 35-38 mg g^{-1}, respectively, were retained in the sheets regardless of DP_w values of PTMMACs. These PTMMAC-N^+ and CMC-COO^- contents in the sheets correspond to ~80% and ~90% retention ratios, respectively; CMC molecules can be retained in the sheets quite effectively by the dual polymer system. Because the surface charges of cellulose fibers and colloidal particles in the cellulose slurry with 5% PTMMAC and 5% CMC were almost zero, suitable charge balances between anionic and cationic groups in the cellulose slurry resulted in such high retention ratios of PTMMAC and CMC in the sheets. The maximum dry tensile strength was obtained for the sheets prepared with 5% PTMMAC and 5% CMC, indicating that the polyion complexes of PTMMAC/CMC electrolytes homogeneously present in the sheets play a role in reinforcing inter-fiber bonds in the sheets. Though the difference in DP_w of PTMMAC between 342 and 6450 had nearly no influence on CMC retention behavior or wet/dry tensile strength, the water-disintegrability of the sheets was significantly affected by the DP_w values of PTMMAC; the lower the DP_w, the clearly higher the water-disintegrability of the sheets. Thus, suitable conditions to manufacture the PTMMAC/CMC/cellulose sheets for wet wipers can be designed based on the results obtained in this study.

5.5 References

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Chapter 6

Influence of chemical structures of anionic polysaccharides on wet strength of cellulose sheets prepared by dual polymer system / Part I: Degree of substitution (DS) of carboxymethyl cellulose

6.1 Introduction

The mechanisms for the carboxymethyl cellulose (CMC)-rich cellulose sheets to have wet strengths when the sheets contained the solution consisting of ethanol, water, and calcium chloride (EtOH/H_2O/$CaCl_2$) with a relatively high water content, were clarified in term of interactions between carboxyl groups of CMC in the sheets and $CaCl_2$ in soaking solution (Chapter 3). From the results of stoichiometrical analyses such as energy dispersive X-ray fluorescence analysis (XRFA) and energy dispersive X-ray spectroscopy attached to a scanning electron microscope (SEM-EDX) for cellulose sheets after soaking treatment in the EtOH/H_2O/$CaCl_2$ solution with various weight ratios, it was clarified that carboxyl groups of CMC, Ca^{2+}, and Cl^- are formed as the CMC-COO$^-$$Ca^{2+}$$Cl^-$ structure and that low dissociation degrees of carboxylate groups of the CMC-COO$^-$$Ca^{2+}$$Cl^-$ structures in the EtOH-containing soaking solutions contribute to the development of wet-strength of the sheets.

However, the influences of DS of CMC on wet-strength of cellulose sheets have not yet been reported. It is well known that physical properties of aqueous CMC solutions depend on the DS value especially when inorganic salts are added to the solution. [1] Thus, the DS of CMC or the amount of the CMC-COO$^-$$Ca^{2+}$$Cl^-$ structures in the sheets probably influences the dry and wet strengths of the sheets to some extent. There may be an optimum DS of CMC for the CMC-containing cellulose sheets as wet wiper sheets disposable in toilet to have both sufficient wet strength in use (wiping) and water-disintegrability after use.

Therefore, in this chapter, the influence of DS of CMC on wet-tensile strength of the CMC-containing cellulose sheets is studied, and the mechanism of wet-strength development of the sheets is discussed based on the obtained results.

6.2 Materials and methods

6.2.1 Materials

See Table 2.1 (Chapter 2) about the characteristics of cellulose fiber and PTMMAC with DP_w 342, which were used in sheet-making. In this chapter, CMC samples with various DS values: 1.29, 0.96, 0.67, 0.63, and 0.49 were used in sheet-making. Fundamental characteristics of CMCs, PTMMAC, and cellulose fiber used in this chapter are listed in Table 2.1 (Chapter 2).

6.2.2 Cellulose sheet-making with PTMMAC and CMC

Cellulose sheets were prepared according to the procedure described in Chapter 3. The addition level of CMC was fixed to 5% based on the dry weight of cellulose fiber. On the other hand, the addition level of PTMMAC was appropriately controlled based on the DS of CMC to be added to cellulose slurries so that a maximum dry-tensile strength was obtained for each PTMMAC/ CMC-containing cellulose sheet except that addition levels of PTMMAC were adjusted to make the cellulose sheets with almost equal dry tensile strength.

6.2.3 Evaluations of the cellulose sheets

Dry and wet tensile strengths of cellulose sheets were evaluated according to the procedure mentioned in Chapters 3 and 5. The water-disintegrabilities of the sheets were evaluated according to the procedure described in Chapter 5.

6.2.4 Analyses

The conformation of CMC in the aqueous solution containing inorganic salt was evaluated by SEC-MALLS according to previously reported methods (Chapter 2). [1), 2)] 0.1M and 0.002M sodium nitrate ($NaNO_3$) aqueous solution were used as the eluents. The PTMMAC-N^+ contents in cellulose sheets were calculated from their nitrogen contents determined by elementary analysis (Chapters 3 and 4). The calcium contents of cellulose sheets were determined using XRFA (Chapter 3). The CMC-COO$^-$ contents in cellulose sheets were calculated according to the method described in Chapter 4.

6.3 Results and discussions

6.3.1 Relationships between dry tensile strength and polymer contents of cellulose sheets

Dry tensile strengths of the cellulose sheets prepared with 0-9% PTMMAC and 5% CMC are depicted in Figure 6.1. As shown in Chapter 5, not only the retention behavior of PTMMAC-N^+ and CMC-COO$^-$ electrolytes but dry tensile strength depends on the

charge balance between anionic and cationic groups present in the cellulose slurries in sheet-making. The amount of PTMMAC required for the highest dry tensile strength of the cellulose sheets increased, as the DS or carboxyl content of each CMC used in the cellulose sheet-making was increased. Although the plots of dry tensile strength for the sheets prepared with CMC of DS 0.67 are not shown in Figure. 6.1, the highest dry strength was 46.1 Nm g^{-1}, when the addition levels of PTMMAC and the CMC were 4.15% and 5%, respectively. Thus, the highest dry strengths were almost equal between the cellulose sheets prepared with CMCs of DS 0.63-1.29.
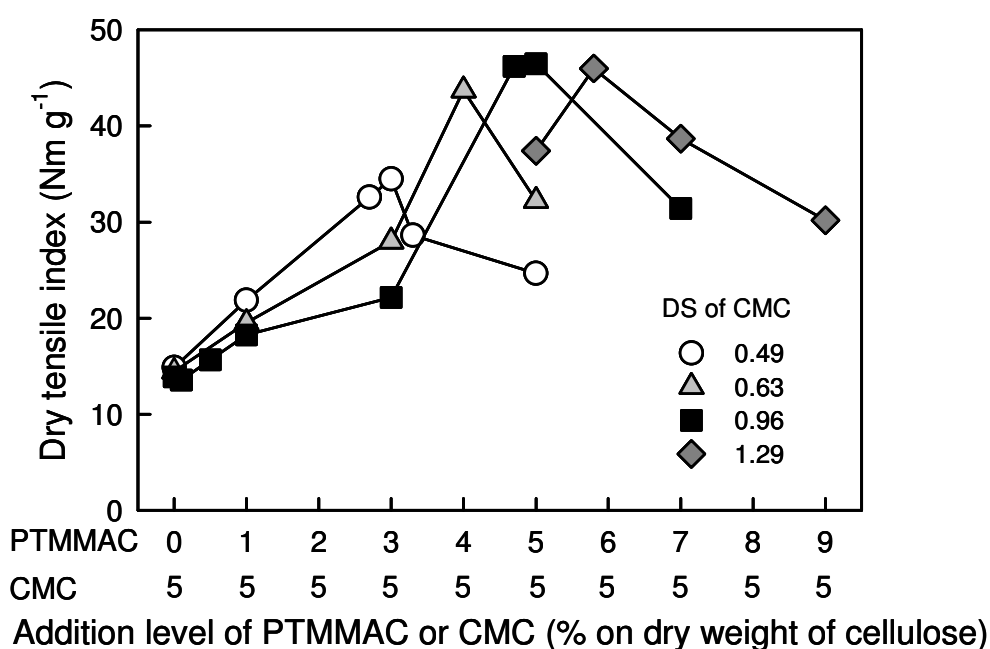

Figure 6.1 Dry tensile strength of cellulose sheets prepared with 0-9% PTMMAC and 5% CMC. The effects of DS of CMCs on dry tensile strength are presented in this figure.

The contents of PTMMAC-N$^+$ and CMC-COO$^-$ polyelectrolytes in the cellulose sheets having the highest dry strengths in Figure 6.1 are shown in Figure 6.2. The CMC-COO$^-$ contents in the cellulose sheets were quite similar to each other irrespective of the DS values. The results in Figure 6.2 show that the highest dry tensile strengths of the cellulose sheets prepared by the PTMMAC/CMC dual polymer system primarily correspond to the CMC contents in the sheets regardless of the DS or DP of the CMCs used in sheet-making except for the CMC with DS 0.49. When CMC with DS 0.49 was used in sheet-making, the highest dry strength was lower than those of the cellulose

sheets prepared with other CMCs. This may be caused by low solubility or clear aggregation behavior of the CMC molecules with DS 0.47 in the tap water used in sheet-making.

Based on the addition levels of PTMMAC-N^+Cl^- and CMC-COO^-Na^+ to cellulose slurries in Figure 6.1, retention ratios of PTMMAC and CMC in the cellulose sheets, i.e. (the amount of PTMMAC-N^+ or CMC-COO^- in the sheets)/(PTMMAC-N^+Cl^- or CMC-COO^-Na^+ added to cellulose slurries)×100, were 60-79% and 73-79%, respectively.

As shown in Table 2.1 (Chapter 2) and Figure 6.2, DP values are different between the CMCs with DS values ranging from 0.63 to 1.29. However, the result in Figure 6.1 shows that neither DP nor DS of CMC having these DS and DP ranges have clear influence on the CMC-COO^- content or the highest dry tensile strength of the cellulose sheets except for the CMC of DS 0.49.
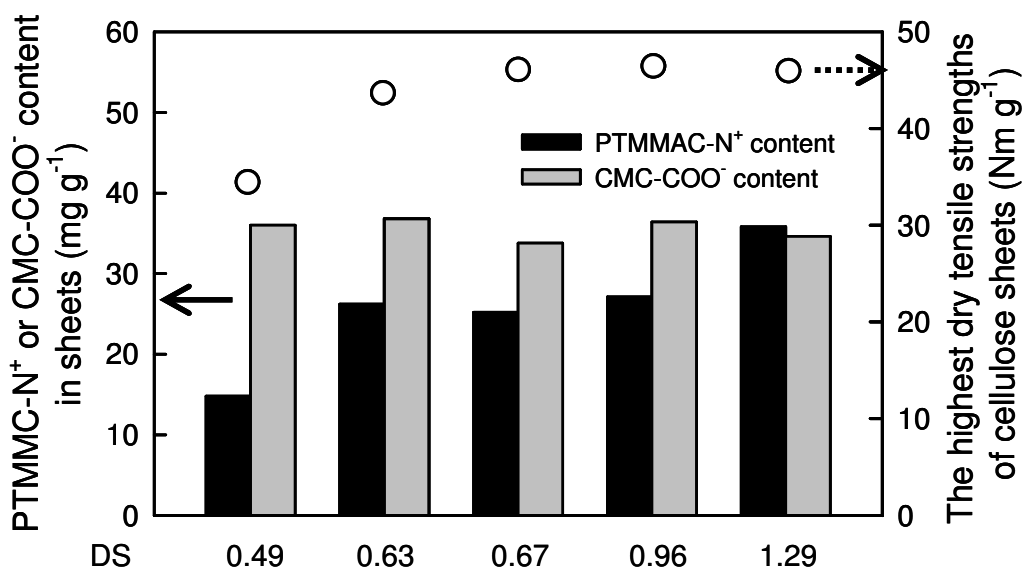

Figure 6.2 PTMMAC-N^+ and CMC-COO^- contents in cellulose sheets having the highest dry tensile strengths in Figure 6.1.

As shown in Figure 2.9 in Chapter 2, the SEC elution pattern and the corresponding MM plots of the CMC with DS 0.49 were different from those of other CMCs, showing that some intra- and/or intermolecular aggregates of CMC molecules were formed and present in the fractions at 6-8 mL elution volume. SEC patterns and MM plots in Figure 2.9 were obtained using the eluent, whose electric conductivity (corresponding to 0.1M

NaNO$_3$ aqueous solution) was larger than that of the tap water used in sheet-making (0.25 mS cm^{-1}, corresponding to 0.002M NaNO$_3$ aqueous solution). Even when the 0.002M NaNO$_3$ aqueous solution was used as the eluent, the SEC pattern and MM plot were similar to those obtained using the 0.1M NaNO$_3$ aqueous solution (Figure 6.3). This indicates that such aggregates of CMC molecules with DS 0.49 observed in Figure 6.3 are likely to be formed and present also in the cellulose slurry used for sheet-making. Because electrostatic repulsions between CMC molecules with DS as low as 0.49 are probably weak in aqueous solutions containing electrolytes (0.002 M NaNO$_3$ in this case), aggregations of CMC molecules have occurred to some extent between the relatively abundant glucosyl units by hydrogen bonds and/or van der Waals interactions. [1), 3)]
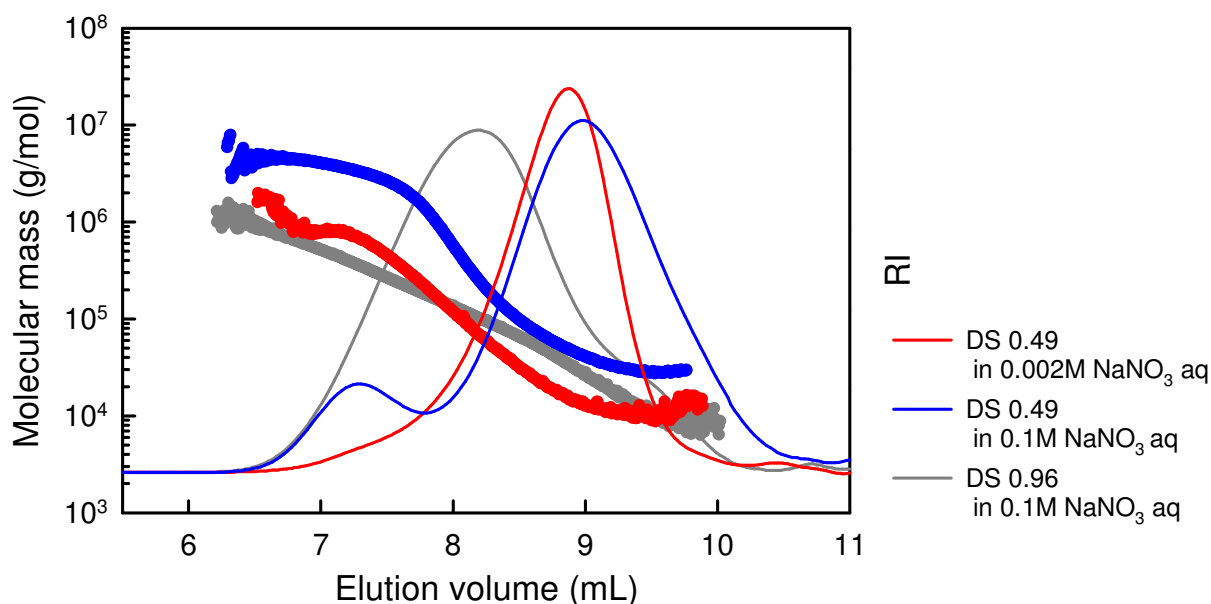

Figure 6.3 SEC elution patterns and the corresponding molecular mass (MM) plots of CMCs, determined at various concentrations of inorganic salt in the elution. The SEC pattern and MM plot of CMC with DS 0.96 is shown as an example of appropriate SEC elution pattern without any aggregates.

The results in Figures 6.1-6.3 indicate that the formation of aggregates of CMC molecules with DS 0.49 in the cellulose slurries has negative impact on the improvement of inter-fiber bonds in the cellulose sheets. It was found in the previous paper that most of anionic CMC molecules added were retained in the sheets, forming

polyion complex particles with cationic PTMMAC molecules during the sheet-making process (Chapter 5). Probably, more even distribution in size of the PTMMAC/CMC polyion complex particles and/or more homogeneous distribution of the polyion complex particles adsorbing on the cellulose fiber surfaces could not be achieved in the sheet-making process, when the CMC of DS 0.49 was added to the cellulose slurries.

On the other hand, main SEC elution peak of the CMC with DS 0.47 was detected at larger elution volume (8-10 mL) than those of other CMCs (Figure 2.9 in Chapter 2 or Figure 6.3). This suggests that the DP of CMC with DS 0.47 is much lower than those of other CMCs. From the SEC pattern, DP of the CMC with DS 0.47 is estimated to be 200-300, though the accurate value cannot be determined because of the presence of a minor peak at smaller elution volume (6-8 mL) and the inappropriate MM plot. Therefore, the CMC with lower DP may have caused the low dry tensile strength of the sheet.

6.3.2 The influence of DS or DP of CMCs on the wet tensile strength

Figure 6.4 shows wet tensile strength of the cellulose sheets prepared with PTMMAC and CMCs with different DS and DP values followed by soaking in EtOH/H_2O/$CaCl_2$ with various weight ratios. Here, the cellulose sheets prepared with the CMC of DS 0.49 were not evaluated because of low dry tensile strength (Figures 6.1 and 6.2). The wet strength decreased with an increase in water content in the soaking solutions for all the cellulose sheets irrespective of the DS or DP values of CMCs, as described in Chapters 3 and 5. However, careful observation of the result in Figure 6.4 reveals that the cellulose sheets prepared with different CMCs had clearly different wet strengths, when they were soaked in the solution consisting of about 20% ethanol. The higher the DS of CMC, the higher the wet strength of the cellulose sheets.

When the EtOH/H_2O/$CaCl_2$ solutions containing water-based detergents are used in the soaking treatment for wet wiper cellulose sheets, the EtOH content is better to be set as low as possible. However, the wet strengths have to be >5 Nm g^{-1} for keeping the sheet form in use (wiping). Thus, CMC with higher DS is better to be used for the wet wiping cellulose sheets. In contrast, no clear difference in dry tensile strength was observed between the cellulose sheets prepared with CMCs having different DS values. When no ethanol was present in the soaking solution, all the CMC-containing cellulose sheets completely lost the wet strengths.
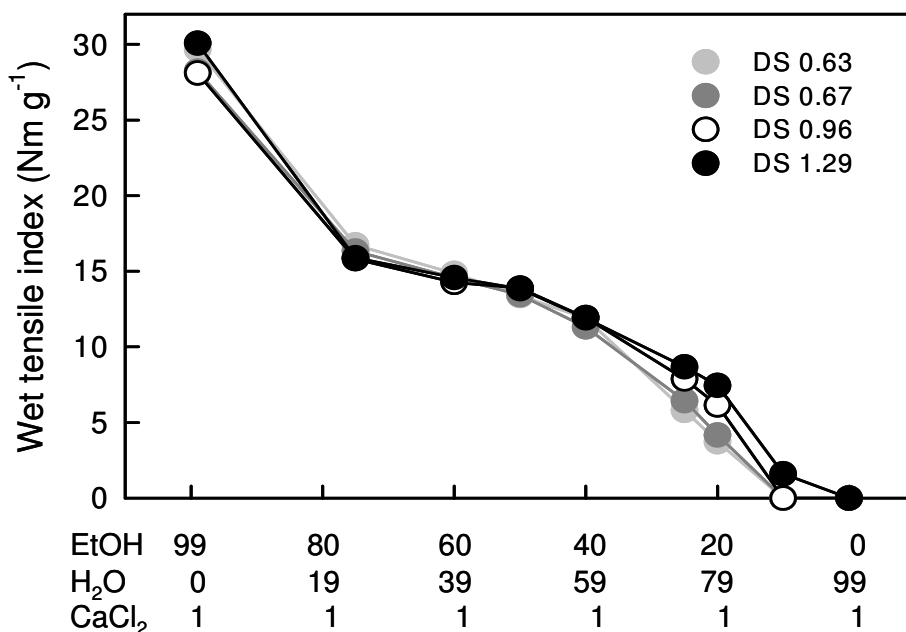
Figure 6.4 Wet tensile strength of cellulose sheets prepared with PTMMAC and CMC (DS 0.63-1.29), when soaked in $EtOH/H_2O/CaCl_2$ solution with various weight ratios.
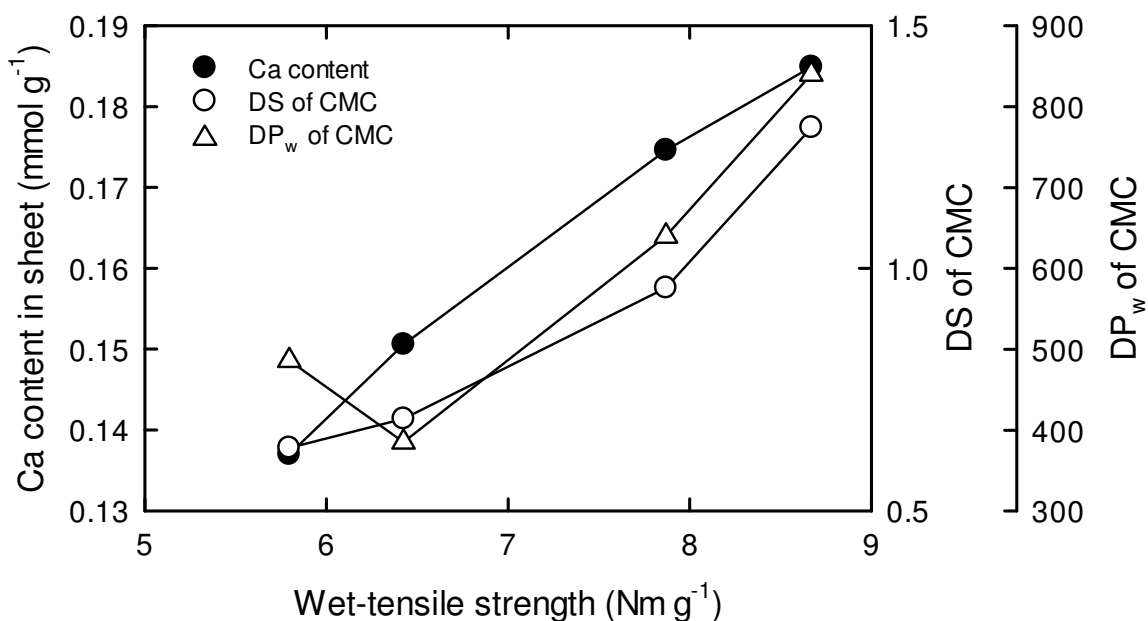

Figure 6.5 Relationships between wet tensile strength of the CMC-containing cellulose sheets after soaking in $EtOH/H_2O/CaCl_2$ with weight ratio of 25:74:1 and either Ca content of the sheets, DS or DP_w of CMCs used in sheet-making.

Figure 6.5 depicts relationships between wet strength of the PTMMAC/CMC -containing cellulose sheets soaked in the EtOH/H_2O/CaCl$_2$ solution with the weight ratio of 25:74:1 and either Ca content of the sheets, DS or DP$_w$ of CMCs used in sheet-making. The results in Figure 6.5 show that the higher the Ca content in the cellulose sheets or the higher the DS of CMC used in sheet-making, the higher the wet strength of the sheets. Thus, the amount of the salt structures CMC-COO$^-$Ca^{2+}Cl$^-$ formed in the cellulose sheets by the soaking treatment in the EtOH/H_2O/CaCl$_2$ solution is likely to contribute to wet strength development.

However, because DP values were also different between CMCs, the results in Figure 6.5 cannot be discussed only in terms of DS of CMCs as a variable. In fact, wet strength of the cellulose sheets increased also with increasing DP$_w$ of CMCs except for the data of the CMC of DS 0.67. Nevertheless, the differences in wet tensile strength of the cellulose sheets were observed between the CMCs used, only when ethanol contents of the soaking solutions were around 20% (Figure 6.4). Thus, it is likely that the DS value rather than DP of CMCs primarily influence the wet strength development of the cellulose sheets, when soaked in the 20% ethanol-containing solutions. If so, CMCs with higher DS values are more appropriate to be used in sheet-making for producing disposable wet wiping cellulose sheets, when the DS values of CMCs range from 0.63 to 1.29.

6.3.3 Other physical properties

Though the water-disintegrability of the cellulose sheets prepared with PTMMAC and CMCs with different DS values was evaluated after the soaking treatment in EtOH/H_2O/CaCl$_2$ solution with the weight ratio of 25:74:1, the sheets disintegrated into cellulose fibers within 30 s, and no difference in the disintegrability was detected between the sheets.

Therefore, as far as CMC with DS 0.63-1.29 is used for wet wiping sheets flushable in toilet bowl, CMC with higher DS value is more appropriate for the sheet items with the wet tensile strength of more than 5 Nm g^{-1} by impregnating the cellulose sheet with the aqueous detergent containing smaller ethanol content (Figure 6.4).

6.4 Conclusion

Dry and wet strengths of cellulose sheets prepared with PTMMAC and CMCs with different DS values (0.49-1.29) were evaluated to study the influence of DS of CMC on

the properties required for wet wiping sheets. There was no clear difference in the highest dry tensile strengths between the cellulose sheets prepared with CMCs with different DS or DP values except for the sheets prepared with CMC of DS 0.49. In contrast, wet strength of the cellulose sheets soaked in the EtOH/H$_2$O/CaCl$_2$ solutions of approximately 20% ethanol content increased as the DS of CMC was increased. The Ca content of the cellulose sheets after soaking treatment in the EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 25:74:1 increased with the DS of CMC used in sheet-making, showing that the amount of CMC-COO$^-$Ca^{2+}Cl$^-$ structures present in the sheets is likely to contribute primarily to the improvement of wet strength of the sheets.

In the next chapter (Chapter 7), the effects of homogeneity of carboxyl groups in the anionic molecules and their chemical structures on wet strength of cellulose sheets are discussed.

6.5 References

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2) Obokata, T., Yanagisawa, M., Isogai, A. *J. Appl. Polym. Sci.* **97**. 2249–2255 (2005).

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Chapter 7

Influence of chemical structures of anionic polysaccharides on wet strength of cellulose sheets prepared by dual polymer system / Part II: Distribution of carboxyl groups and chemical structures of main chains

7.1 Introduction

In Chapter 6, the influence of DS of carboxymethyl cellulose (CMC, Figure 2.4 in Chapter 2) on physical properties such as wet strength of CMC-rich cellulose sheets prepared by the dual polymer system was studied. When the composition of the soaking solution (EtOH/H$_2$O/CaCl$_2$ solution) was relatively water-rich (74-79 weight %), wet tensile strength of the sheets increased with increasing DS of CMC (Figures 6.4 and 6.5 in Chapter 6). The obtained results showed that the amount of the CMC-COO$^-$Ca^{2+}Cl$^-$ structure formed between CMC in the sheets and CaCl$_2$ in the soaking solution by the soaking treatment contributed to the development of wet tensile strength of the sheets, and that the formation of such salt structures promoted insolublization of the CMC in the soaking solution (containing EtOH). When the sheets were soaked in the EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 0:99:1, wet strengths of the sheets were completely lost, irrespective of DS of CMC, because of sufficient dissociation of the CMC-COO$^-$Ca^{2+}Cl$^-$ structures in water. Thus, CMC-containing cellulose sheets have unique characteristics.

There are some anionic polysaccharides with carboxylate groups, such as sodium polyuronates. Sodium alginate (ALG) is a well known copolyuronate isolated from brown seaweeds and certain bacteria, which consists of 1,4-linked anhydro-β-D-mannuronate (M) blocks and 1,4-linked anhydro-α-L-guluronate (G) blocks (Figure 2.5 in Chapter 2). [1), 2)] ALG is widely applied to food and pharmaceutical industries. When divalent cations such as Mg^{2+} and Ca^{2+} are added to ALG aqueous solutions, gels are easily formed in short times by the formation of some junction zones. [3), 4)] On the other hand, when divalent cations as described above are added to CMC aqueous solutions, gel is not formed and the original liquid state is maintained though the mobility of CMC molecules in the solutions may be changed to some extent. [5)] Therefore, it is significant to discuss some differences between ALG and CMC-containing cellulose sheets in terms of physical properties of the sheets.

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Additionally, in our group, sodium β-1,4-polyglucuronate (sodium cellouronate, CUA) was obtained by TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical)-mediated oxidation of regenerated and mercerized celluloses at room temperature, and CUA is a water-soluble polyuronate (Figure. 2.6 in Chapter 2). [6] Though physical properties of CUA have not been reported enough, CUA obtained by 4-acetoamide-TEMPO-mediated oxidation at pH 5.8 had a large DP_w comparable to CMC as the paper strength additive from the results of preliminary experiments. Therefore, physical properties of CUA-containing sheets when treated in the EtOH/H_2O/$CaCl_2$ solution like CMC-containing sheets are interesting.

In this chapter, cellulose sheets containing anionic polysaccharides such as CMC, ALG and CUA are prepared with a cationic polymer, using a papermaking technique (dual polymer system). [7-9] Physical properties such as wet strength and water-disintegrability of the obtained sheets are compared. Differences of the physical properties between these sheets are discussed in terms of interactions between carboxylate groups of anionic polysaccharides in sheets and the components of the soaking liquid. Furthermore, the influence of regioselectivity of the carboxylate groups in anionic polysaccharides on the physical properties of the sheets is also discussed.

7.2 Materials and methods

7.2.1 Materials

A commercial softwood bleached kraft pulp without beating was used as the cellulose fiber in sheet-making. A sodium carboxymethyl cellulose (CMC, Figure 2.4 in Chapter 2) with inorganic salt free was kindly provided by Daiich-Kokyo Seiyaku Co., Ltd., Japan, and its DS was 0.96. The CMC used in this chapter is corresponding to the CMC-2 in Table 2-1 in Chapter 2. A sodium alginate (ALG, Figure 2.5 in Chapter 2) was purchased from Wako Pure Chemicals Co., Japan. A sodium β-1,4-polyglucuronate (sodium celluronate; CUA, Figure 2.6 in Chapter 2) was prepared by 4-acetoamido-TEMPO mediated oxidation of regenerated cellulose at pH 5.8. [10] A poly[*N,N,N*-trimethyl-*N*-(2-methacryloxylethy) ammonium chloride] (PTMMAC, Figure 2.1 in Chapter 2) with DP_w 342 was prepared according to the methods as described in Chapters 2. The PTMMAC used in this chapter is corresponding to the PTMMAC-1 in Table 2-1 in Chapter 2. One % (w/v) solutions of CMC, ALG, CUA and PTMMAC were prepared with distilled water, and used as additives in sheet-making process. Other chemicals and solvents were of laboratory grade (Wako Pure Chemicals

Co., Japan) and used as received. The fundamental characteristics of anionic polysaccharides, PTMMAC, and cellulose fiber used in this chapter's study were evaluated by the methods mentioned in Chapter 2, and are listed in Table 2.1 in Chapter 2.

7.2.2 Cellulose sheet-making with PTMMAC and anionic polysaccharides (CMC, ALG, or CUA)

Cellulose sheets were prepared according to the procedure described in 3.2.2. The addition levels of anionic polysaccharides were respectively 5% based on the dry weight of the cellulose. The addition level of PTMMAC was 5% based on the dry weight of the cellulose when CMC solution was added afterwards. When ALG or CUA solution was added, the addition level of PTMMAC was 6% based on the dry weight of the cellulose.

7.2.3 Soaking of the cellulose sheets in ethanol-containing solutions and evaluations

Wet tensile strengths of cellulose sheets after soaking in mixtures of $EtOH/H_2O/CaCl_2$ with various weight ratios were measured according to the procedure described in Chapter 3, and water-disintegrabilities of the sheets were evaluated according to the procedure described in Chapter 5.

7.2.4 Analyses

The PTMMAC-N^+ contents in cellulose sheets were calculated from their nitrogen contents determined by combustion-type gas-chromatography (Chapters 3 and 4). The calcium and chlorine contents of cellulose sheets were determined using a X-ray fluorescence analyzer (XRFA) according to the procedure described in Chapter 3. Solution-state ^{13}C NMR spectra of anionic polysaccharides dissolved in deuterium water (D_2O, Wako Pure Chemicals Co.) were recorded using a JEOL ALPHA-500 spectrometer (JEOL, Japan). [10] 3-Trimethylsilyl-2,2,3,3-d_4-propionic acid sodium salt (Aldrich, USA) was used as an internal standard at 0 ppm. For CMC, solution-state ^1H-NMR spectrum of the CMC, which was hydrolyzed at 80 °C with 25% deuteron sulfuric acid (D_2SO_4, Wako Pure Chemicals Co.) in D_2O, was also recorded using a the same type spectrometer as solution state ^{13}C-NMR. [11] Acetic acid (Wako Pure Chemicals Co.) was used as an internal standard at 2 ppm.

7.3 Results and Discussions

7.3.1 Characteristics of anionic polysaccharides and PTMMAC used in sheet-making

Fundamental characteristics of the PTMMAC, CMC, ALG, CUA and cellulose fiber used in this study are listed in Table 2.1 (Chapter 2). The anionic charge density of ALG calculated from its molecular formula is 5.05 meq. g^{-1}, which was close to the carboxyl content 5.09 mmol g^{-1} determined by the conductivity titration method but was higher than that (4.60 meq. g^{-1}) determined by the charge density determination. Because ALG consists of only uronic acids (anhydro-β-D-anhydro-mannuronic acid and anhydro-α-L-guluronic acid) (Figure 2.5 in Chapter 2), the difference between charge density and carboxyl content of ALG is due to the difference of molecular chain backbones between ALG and PDADMAC.

The anionic charge density of CUA calculated from its molecular formula is also 5.05 meq. g^{-1}, which is clearly higher than the carboxyl content 4.60 mmol g^{-1} determined by the conductivity titration method. The obtained results indicate that some C6 primary hydroxyl groups, which were not oxidized to carboxylates, probably remained in the obtained CUA. [10] However, major component of the obtained CUA (that was corresponding to the main SEC peak in Figure 2.9 of Chapter 2) was water-soluble, and no residual C6 primary hydroxyl group in CUA was detected at least in the solution-state of ^{13}C-NMR spectrum (Figure 7.1 (a)). Therefore, the carboxyl content and the charge density obtained by titration methods are naturally different from the calculated value, and the difference between both experimental values are also attributed to the difference of molecular chain backbone structures between CUA and PDADMAC in a similar manner between ALG and PDADMAC.

In the case of CMC, not only the difference of molecular chain backbone structures but also the heterogeneous distribution of carboxymethyl (CM) substituents along one CMC molecule may have caused such difference in the values between charge density and carboxyl content. [12] Figure 7.2 shows ^{1}H-NMR spectrum of the hydrolyzed CMC with DS 0.96. As the result analyzed in accordance with the method of Tuyet *et al.*, the distribution of CM substituents at C2, C3, and C6 positions were determined to be in the molar ratio of CM(C2)/CM(C3)/CM(C6) = 41/20/39. [11] The influence of regioselectivity of the carboxylate groups in anionic polysaccharides on the physical properties of the sheets is discussed in the following sections of this chapter.
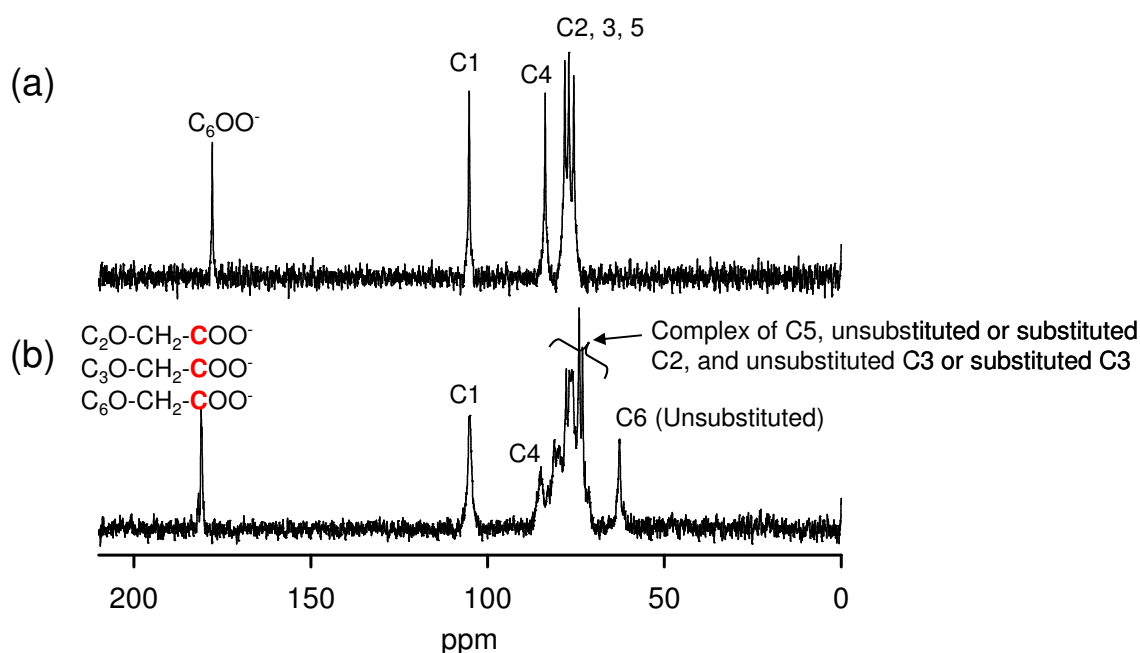
Figure 7.1 ^{13}C NMR spectra of anionic polysaccharides in D_2O, a) CUA b) CMC (DS=0.96, reference of CUA), with corresponding signal assignments.

In this study, CMC-, ALG-, and CUA-containing sheets (CMC, ALG and CUA sheets) were prepared, in which the addition levels of CMC, ALG, and CUA to cellulose slurries were fixed to 5% on dry weight of the cellulose, and the addition levels of PTMMAC were 5% for CMC sheet and 6% for ALG and CUA sheets. The addition levels of PTMMAC were adjusted so that the obtained sheets could have maximum dry-tensile strength as the sheets prepared with anionic polysaccharides of 5% addition level (Chapter 5 and 6). When 1g cellulose exists in the PTMMAC/CMC/cellulose slurry subjected to the sheet-making, the amount of cationic groups due to PTMMAC present in the slurry was 0.238 mmol and that of total anionic groups originating from CMC and the cellulose surface were calculated to be 0.209 mmol. When 1g cellulose exists in the PTMMAC/ALG/cellulose slurry, the amount of cationic groups of PTMMAC was 0.285 mmol and those of total anionic groups due to ALG and the cellulose surface were 0.262 mmol. When 1g cellulose exists in the PTMMAC/CUA/cellulose slurry, the amount of cationic groups of PTMMAC was 0.285 mmol and those of total anionic groups due to CUA were 0.237 mmol. Thus, the PTMMAC/anionic polysaccharide/cellulose slurry was set to be slightly rich in cationic groups. Because the surface charge of the cellulose fiber was only 0.007 meq. g^{-1}, all carboxylate groups of anionic polysaccharides should form amine salts with PTMMAC,

forming polyion complexes. Details of retention mechanisms of PTMMAC and CMC molecules on the cellulose sheets in sheet-making process and their structures of polyion complexes are discussed in Chapter 5. The retention mechanisms of PTMMAC and the other anionic polysaccharides on the cellulose sheets are likely to be similar to those in the case of PTMMAC/CMC/cellulose sheets.
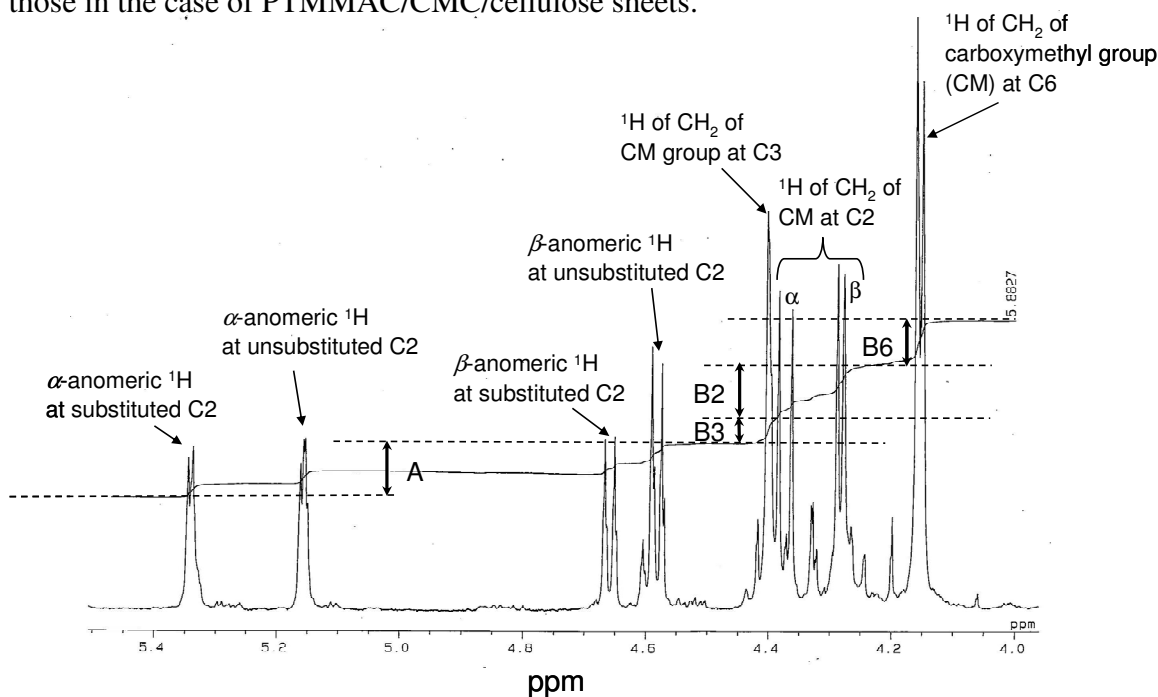

Figure 7.2 ^{1}H NMR spectrum of the CMC (DS=0.96) hydrolyzed in 25% D_2SO_4 in D_2O with corresponding signal assignments. The distribution of CM substituents at C2, C3, and C6 positions can be calculated from the peak areas of methylene protons at C2, C3, and C6. When the peak area of methylene protons at C2, C3, and C6 are respevtively, B2, B3, and B6, the distribution of CM substituents at Cx is determined by Bx/(B2+B3+B6) (x=2, 3, or 6). [11]

7.3.2 Wet-tensile strength of ALG sheets soaked in EtOH/H$_2$O/CaCl$_2$ solutions, compared with those of CMC sheets

The ALG sheets were soaked in either EtOH/H$_2$O/CaCl$_2$ solutions (Solutions A) or EtOH/H$_2$O solutions (Solutions B) with various weight ratios of the components for 30 min, and the wet-tensile strengths were immediately measured without drying (Figure 7.3). When ALG sheets were soaked in Solution B, the wet strengths of the sheets increased as the EtOH content of the soaking solution was increased in the similar

manner to those of CMC sheets. The wet-tensile strength of ALG sheets increased to 15 Nm g^{-1} when soaked in 100% EtOH, because inter-fiber hydrogen bonds present in the sheets and their contributing to sheet strengths are maintained even by soaking the sheets in solutions rich in EtOH. Thus, the formation of polyion complexes between PTMMAC and ALG molecules in the cellulose sheets explicitly led to the wet-strength improvement probably by reinforcing effect of inter-fiber bonds. The wet strength decreased as the H_2O content of Solution B was increased, and no wet strengths were detected when 100% H_2O was used as the soaking solution. However, wet-tensile strengths of ALG sheets were lower than those of CMC sheets when these sheets were soaked in Solution B. Indeed, the dry-tensile strength of ALG (27.1 Nm g^{-1}) sheet was lower than that of CMC sheet (46.5 Nm g^{-1}), which, in fact, leads to the difference of the wet strengths between those two sheets. This may be essentially attributed to the difference of cohesive force between CMC and ALG or to that ALG contents in ALG sheets are lower than CMC contents in CMC sheets.
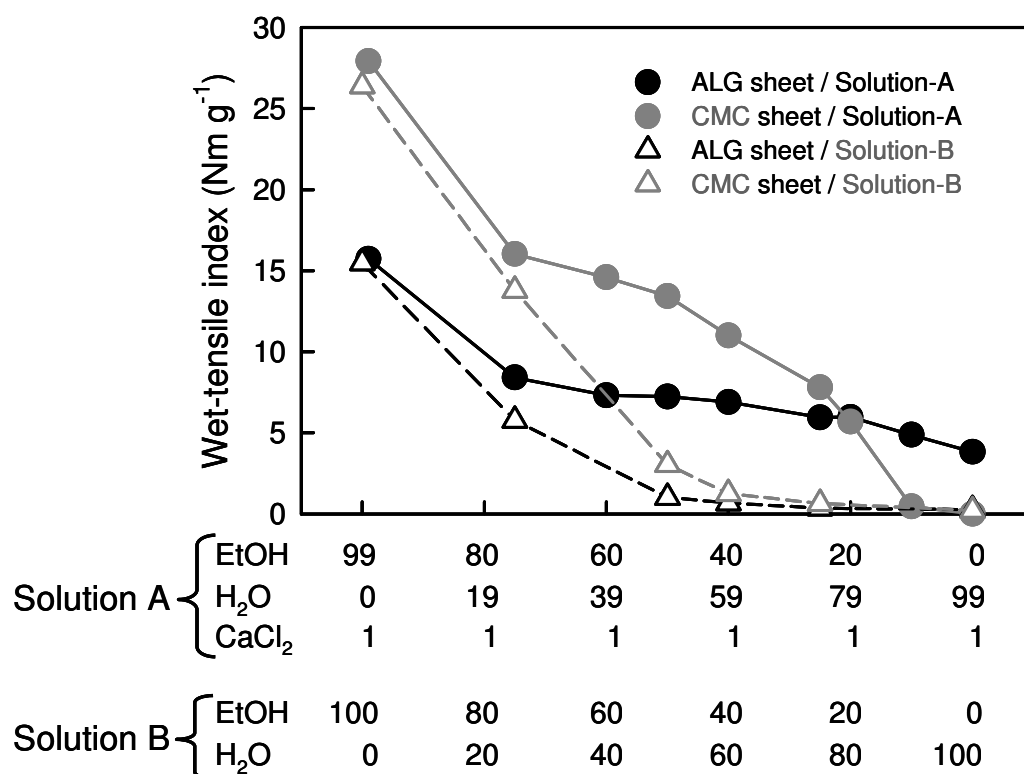

Figure 7.3 Relationships between weight ratios of the soaking solution components and wet tensile strength of ALG or CMC sheets soaked in the solutions.

On the other hand, when ALG sheets were soaked in Solutions A containing 1% $CaCl_2$, a different wet strength pattern was observed particularly for the Solutions A with EtOH contents from 60% to 0%. The presence of 1% $CaCl_2$ in the soaking solutions remarkably improved wet-tensile strengths of the sheets in this range of EtOH contents. When water content in Solutions A was less than 80%, the wet tensile strengths of CMC sheets were higher than those of ALG sheets. However, when the CMC and ALG sheets were soaked in Solutions A containing more than 80% water, ALG sheets had higher wet tensile strengths than for CMC sheets. ALG sheet had wet strength of 3.8 Nm g^{-1} even in the Solution A containing no EtOH and completely maintained its sheet form, although CMC sheet completely lost its strength and partially disintegrated in the solution (Chapter 3 or 5). Water contents of Solutions A had less influence on the wet tensile strengths of ALG sheets than those of CMC sheets, when water contents were more than 19%.

Therefore, the mechanisms for ALG sheets to have wet tensile strengths in Solutions A may be different from those for CMC sheets. Details are discussed later.

7.3.3 Wet-tensile strength of CUA sheets soaked in EtOH/H$_2$O/CaCl$_2$ solutions, compared with those of CMC sheets

The CUA sheets were treated in the same way as ALG or CMC sheets in either Solutions A or B, and the wet-tensile strengths were immediately evaluated (Figure 7.4). The effect of the composition of the soaking solutions (Solutions A and B) on the wet-tensile strengths of CUA sheets was similar to that on the wet-tensile strengths of ALG or CMC sheets; the wet strengths of the sheets were improved by the presence of 1% $CaCl_2$ in the soaking solution. However, CUA sheets had much higher wet-tensile strengths than for CMC sheets, when soaked in Solutions B with EtOH contents from 60% to 25% without $CaCl_2$. These phenomena were also different from those shown in ALG sheets treated similarly in Solution B (Figure 7.3). When CUA sheet was soaked in the Solution A with 0% EtOH, the sheet had wet-tensile strength of 3.2 Nm g^{-1} and kept its sheet form completely unlike the CMC sheet treated under the same condition. The obtained results show that the mechanisms for CUA sheets to have wet-tensile strengths after the soaking treatment in Solution A or B may be different from those for CMC and ALG sheets.
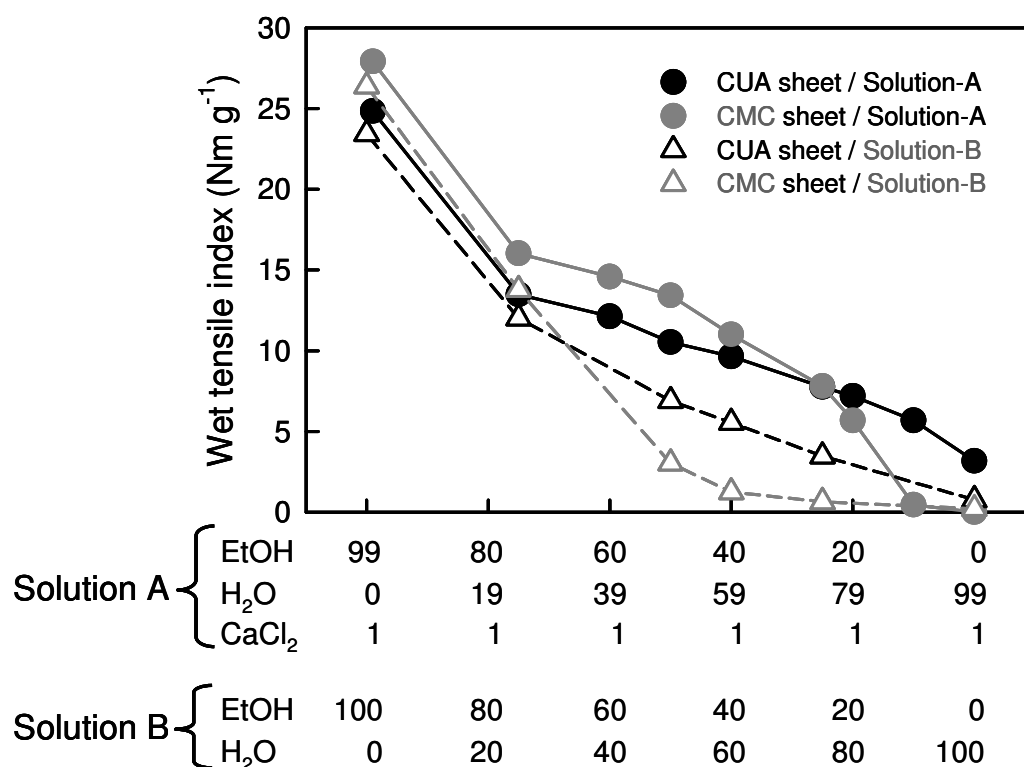
Figure 7.4 Relationships between weight ratios of the soaking solution components and wet tensile strength of CUA or CMC sheets soaked in the solutions.

7.3.4 Determination of PTMMAC-N$^+$, Ca^{2+} and Cl$^-$ contents in cellulose sheets and structures of PTMMAC, CMC, ALG, and CUA molecules in the sheets before and after soaking treatments

The PTMMAC, calcium and chloride contents in the sheets before and after the soaking treatments in Solutions A should be determined in order to explain the mechanism of wet strength appearance for ALG and CUA sheets shown in Figures 7.3 and 7.4. Figure 7.5 shows the contents of PTMMAC-N$^+$ ions of the sheets before and after the soaking treatment in Solutions A with different EtOH/H$_2$O/CaCl$_2$ weight ratios, and these contents were calculated from nitrogen contents of the sheets determined by elementary analyses. [11] Because PTMMAC-N$^+$ molecules are insoluble in EtOH, almost all PTMMAC-N$^+$ molecules present in the original sheets remained in the sheets even after soaking in Solutions A with 99% and 75% EtOH contents, and the PTMMAC-N$^+$ contents ranged approximately from 29 to 35 mg g^{-1}. As shown in the CMC sheets, the water-soluble PTMMAC-N$^+$ molecules were prone to be removed as PTMMAC-N$^+$Cl$^-$ molecules from the ALG sheets and the CUA sheets as the H$_2$O

content of Solutions A was increased. The PTMMAC-N$^+$ contents became lower than 2 mg g^{-1}, when the EtOH contents of the soaking solution were lower than 25%. Thus, more than 93% of PTMMAC-N$^+$ molecules originally present in the cellulose sheets were removed from the sheets by soaking in the water-rich solutions. These results indicate that cationic PTMMAC-N$^+$ molecules, which are present in the original cellulose sheets forming polyion complexes mostly with anionic polysaccharide-COO$^-$ molecules, became soluble in water-rich soaking solutions containing CaCl$_2$ by exchanging their counter ions from carboxylate groups to Cl$^-$ ions during the soaking treatment.
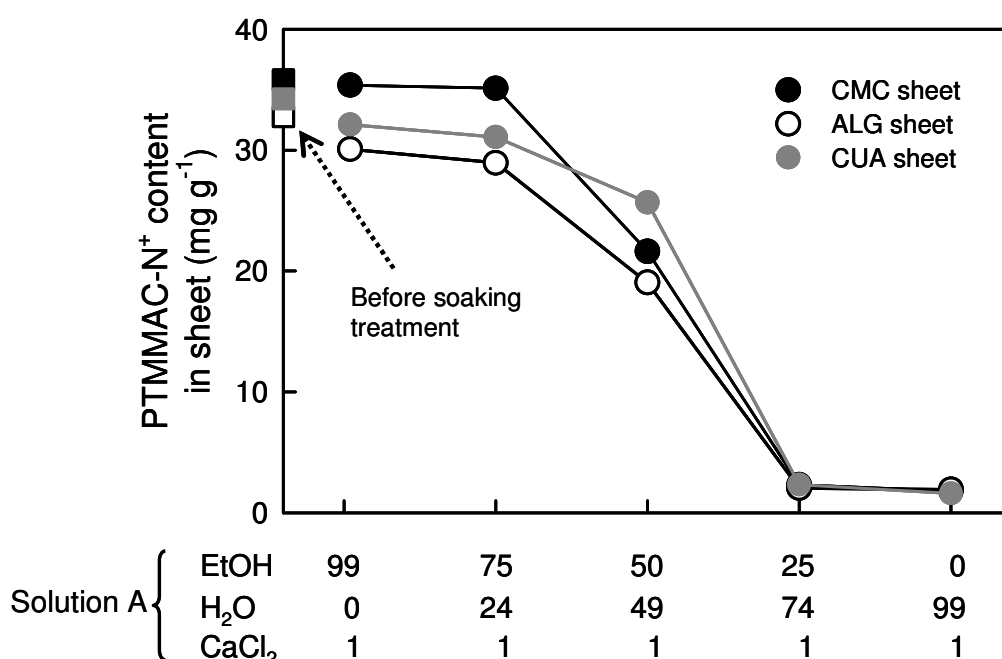
Figure 7.5 PTMMAC-N$^+$ contents of the cellulose sheets soaked in Solutions A with different weight ratios of the three components and then washed thoroughly with fresh EtOH to remove excess CaCl$_2$.

Calcium contents of the sheets soaked in Solutions A and then washed thoroughly with fresh EtOH to remove excess CaCl$_2$ were determined by XRFA, and depicted in Figure 7.6. In the case of the blank cellulose sheets prepared without PTMMAC or anionic polysaccharides, calcium contents corresponded well to the carboxyl content of the cellulose fiber (0.06 mmol g^{-1}), which were determined by the conductivity titration method (Table 2.1 in Chapter 2). This result indicates that CaCl$^+$ ions were present as the counter ions of all carboxyl groups present in the blank cellulose sheets, forming the

structure of cellulose-COO$^-$Ca^{2+}Cl$^-$ but not the cross-linked structures like (cellulose-COO$^-$)$_2$Ca^{2+} (Chapter 3).
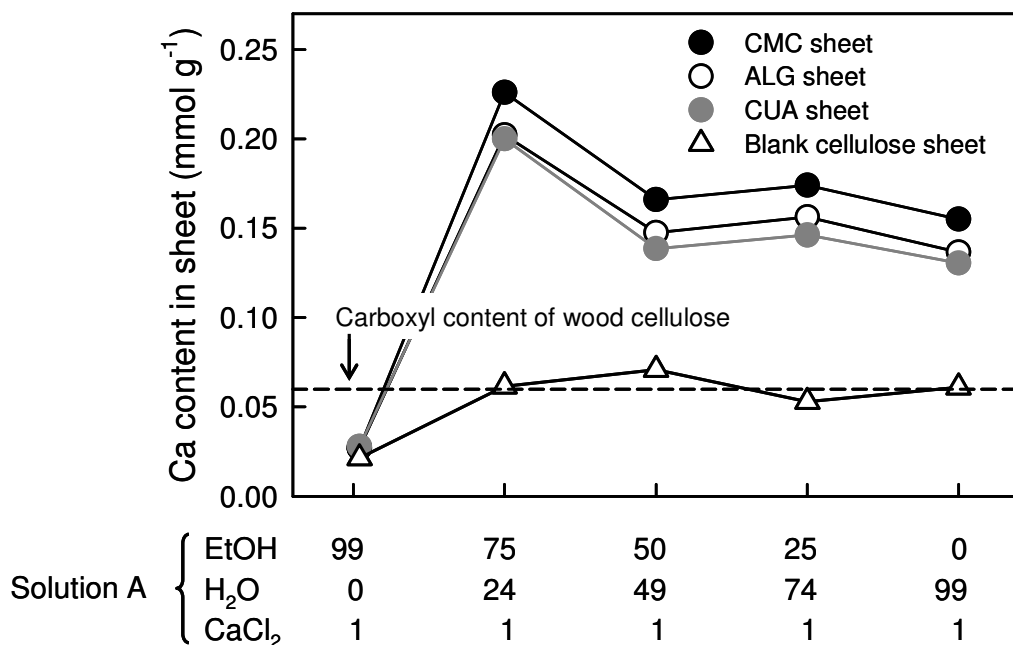

Figure 7.6 Calcium contents of cellulose sheets soaked in Solutions A with different weight ratios of the three components and then washed thoroughly with fresh EtOH to remove excess CaCl$_2$.

When each cellulose sheet was soaked in Solutions A, the maximum calcium content was observed, when the weight ratio of the soaking solution EtOH/H$_2$O/CaCl$_2$ was 75:24:1 (Solution A-75:24:1). The calcium contents decreased to approximately 0.14-0.17 mmol g^{-1}, when the soaking solutions with EtOH contents of 0-50%. In these cases, some fibers in these sheets were partly removed during stirring in fresh EtOH after soaking in Solutions A so that a part of fine particles of PTMMAC/anionic polysaccharide polyion complexes may have been separated from the cellulose fiber and lost during washing process by filtration. When Solution A-75:24:1 was used as the soaking solution, on the other hand, the sheet form was stably maintained in all cases examined. Based on the results in Figures 7.5 and 7.6, almost all PTMMAC and anionic polysaccharide molecules present in the original sheets remained in the sheets after soaking in Solution A-75:24:1. Calcium contents of CMC sheets strongly correlate with CMC contents of the sheets (Chapter 3). Therefore, calcium contents of ALG and CUA sheets may be also related to ALG and CUA contents, respectively. In order to

determine ALG or CUA contents of these sheets, it is important to estimate the structures formed between carboxyl groups of ALG or CUA in sheets, Ca^{2+}, and Cl^-.
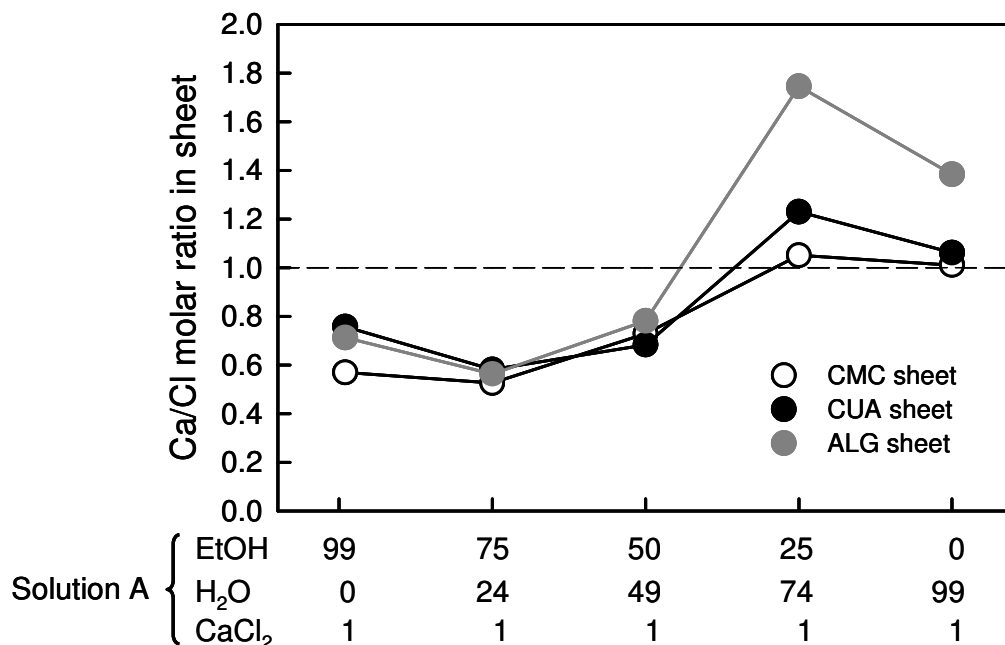

Solution A	EtOH	99	75	50	25	0
	H_2O	0	24	49	74	99
	$CaCl_2$	1	1	1	1	1

Figure 7.7 The effect of composition of Solutions A on Ca/Cl molar ratios of anionic polysaccharide-containing sheets.

Figure 7.7 displays the effect of composition of Solutions A components on Ca/Cl molar ratios of all cellulose sheets. Ca/Cl molar ratio in each sheet was also determined by XRFA. When ethanol content was high enough, i.e. 99%-75%, the moles of Cl^- in all sheets were more than those of Ca^{2+} because most of all PTMMAC-N^+Cl^- molecules remained in the sheets as shown in Figure 7.5. This indicates that chloride ions are present in all sheets as counter ions of both PTMMAC-N^+ and carboxyl groups of CMC, ALG, or CUA.

However, PTMMAC-N^+ contents of the sheets decreased with increasing water content in Solutions A, and most of PTMMAC-N^+ molecules were removed from the sheets especially when water content in Solutions A was more than 74% (Figure 7.5). In the case of CMC sheets, the mole of calcium ions became equal to those of chloride ions. On the other hand, in ALG or CUA sheets, the contents of calcium ions became more than those of chloride ions (Figure 7.7). This result revealed that the structures formed in CMC sheets between Ca^{2+}, Cl^- and carboxyl groups of CMC molecules is partly different from those formed in ALG or CUA sheets. In CMC sheets, carboxyl

groups of CMC molecules in the sheets may form $–COO^-Ca^{2+}Cl^-$ structures alone with calcium ions and chloride ions in Solutions A, whereas, in ALG or CUA sheets, carboxyl groups of ALG or CUA are likely to form not only $–COO^-Ca^{2+}Cl^-$ structures but also cross-linked structures like $(–COO^-)_2Ca^{2+}$.

7.3.5 The water-disintegrabilities of anionic polysaccharide sheets

Figure 7.8 shows the photo images of each cellulose sheet after the water-disintegration test. Every photo was taken until 1 min later after dropping the sheet in the stirred water. Before the water-disintegration test, each cellulose sheet was treated in the Solution A whose weight ratio EtOH/H_2O/$CaCl_2$ was 25:74:1 (Solution A-25:74:1). The CMC sheet was completely disintegrated to cellulose fiber in water within 25 s, whereas ALG and CUA sheets did not disintegrate 1 min later after dropping these sheets in water. These sheets were not disintegrated even 10 min later after the dropping. The sheets were apparently little damaged during the water-disintegration test, and maintained their original sheet forms (Figure 7.9). The obtained results indicate that ALG and CUA sheets do not have water-disintegrabilities due to the formation of stable bonds in water between Ca^{2+} and carboxyl groups of ALG or CUA.

7.3.6 The effect of structures of CMC, ALG, and CUA molecules retained in the sheets after soaking treatments on the wet-tensile strengths and the water-disintegrabilities of the sheets

The wet-strengths of ALG and CUA sheets were 3.8 and 3.2 Nm g^{-1}, respectively, after the soaking treatment in Solution A consisting of 99% water and 1% $CaCl_2$, though the wet-strengths of CMC sheets were completely lost (Figure 7.3 or 7.4). CMC sheets treated in Solution A-25:74:1 were easily disintegrable in water, while ALG sheets and CUA sheets treated similarly maintained their original sheet forms without being disintegrated in water (Figure 7.8 or 7.9). Therefore, it is reasonable to assume that some stable bonds to water were formed between Ca^{2+} and carboxylate groups of ALG or CUA in sheets. From these results, carboxyl groups of ALG or CUA in the sheets may form not only $–COO^-Ca^{2+}Cl^-$ structures but also cross-linked structures like $(–COO^-)_2Ca^{2+}$. Such cross-linked structures are stable to water. However, the real cross-linked structures between carboxyl groups and Ca^{2+} may be more complicated. For examples, ALG is well-known as a linear polyuronate that can form a gel with
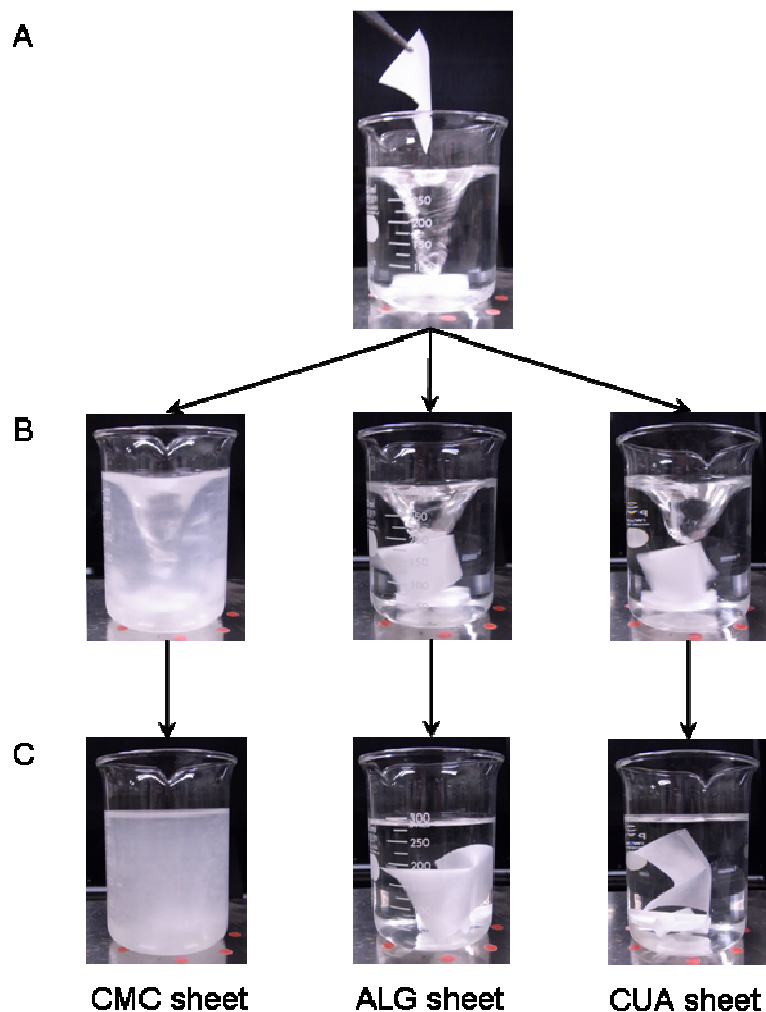
Figure 7.8 Photo images of cellulose sheets subjected to the water-disintegration test according to JIS P4501 (1993). A: cellulose sheet before the test, B: the sheets 15 s later after dropping them in the stirred water, C: the sheets when the water-stirring was stopped 1 min later after dropping them in the stirred water.
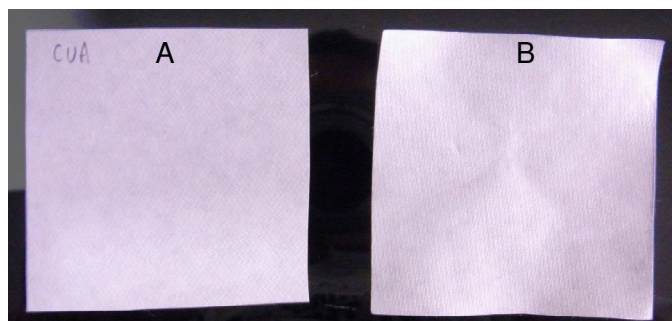

Figure 7.9 Photo images of CUA sheets before and after the water-disintegration test according to JIS P4501 (1993). A: CUA sheet before the test, B: the sheet 8 min later after dropping it in the stirred water.

divalent metal ions such as Ca^{2+}. [3] The egg-box binding has been proposed for the formation between ALG molecules (anhydro-α-L-guluronate blocks) and Ca^{2+} ions. [3, 14] The egg-box binding model has been extensively and thoroughly studied by a lot of workers for many years. [2, 4, 13] Thus, ALG molecules in the sheets might also form such a structure when the sheets were soaked in the solutions A. As the results, wet tensile strengths of the Ca^{2+}-retained ALG sheets might appear even in water, leading to the non-water-disintegrability. However, as described above, the positive wet tensile strengths of CUA sheets after the soaking treatment in the solution A consisting of water and $CaCl_2$ also appeared even in water (Figures. 7.4, 7.8 and 7.9). As indicated in Figures 2.5 and 2.6 (Chapter 2), CUA is the sodium polyuronate consisting of sodium anhydro-β-D-glucuronates similar to the chemical structure of sodium anhydro-β-D-manuronates of ALG. Therefore, it is assumed that some cross-linked structures such as $(–COO^-)_2Ca^{2+}$ are also formed between carboxylates groups of ALG or CUA in the sheets and $CaCl_2$ while some $–COO^-Ca^{2+}Cl^-$ structures were formed between them. However, the distribution of $–COO^-Ca^{2+}Cl^-$, $(–COO^-)_2Ca^{2+}$, and other structures in ALG or CUA sheets cannot be estimated only by Ca^{2+} and Cl^- contents in the sheets, and also accurate ALG and CUA contents in the sheets could not be calculated.

  Unlike in the case of CMC, ALG and CUA have similar chemical structures having C6-carboxylate groups in monomer units so that ALG and CUA molecules in cellulose sheets form some different structures from those of CMC between carboxylate groups and Ca^{2+}. ALG and CUA have only one carboxylate group at every C6 carbon so that their chemical structures are relatively homogeneous. On the other hand, CMC has carboxylate groups somewhere at C2, C3, and C6 carbons, and the distribution of carboxylate groups at C2, C3, and C6 positions were determined to be in the molar ratio of C2/C3/C6 = 41/20/39 (Figure 7.2). [11, 16, 17] The average DS value of CMC subjected to this study was 0.96, and this value is almost equal to carboxylate content of ALG or CUA. However, some monomers of CMC may have no carboxylate group while others have more than one carboxylate group. Thus, CMC is a polymer with heterogeneous chemical structures, which may have resulted in the simultaneous pursuit of the wet strength and water-disintegrability. When CMCs with DS value of more than 2 are retained in cellulose sheets, they may form some cross-linked structures between carboxylate groups and Ca^{2+} after the soaking treatment in Solutions A. [5, 16] Someday, this point will have to be discussed in detail by the author.

7.4 Conclusion

ALG or CUA molecules in the cellulose sheets may form not only $-COO^-Ca^{2+}Cl^-$ structures but also some cross-linked structures such as $(-COO^-)_2Ca^{2+}$, when the sheets soaked in EtOH/H$_2$O/CaCl$_2$ solution. Such cross-linked structures may lead to the appearance of wet strength even in the EtOH/H$_2$O/CaCl$_2$ solution with "no ethanol" and the disappearance of water-disintegrability in ALG or CUA sheets, because cross-linked structures such as $(-COO^-)_2Ca^{2+}$ are stable to water. On the other hand, CMC molecules in the sheets form $-COO^-Ca^{2+}Cl^-$ structures alone when the sheets soaked in EtOH/H$_2$O/CaCl$_2$ solution, leading to the development of wet strength in the EtOH/H$_2$O/CaCl$_2$ solution with "some ethanol" and the appearance of disintegrability in stirred water. Because $-COO^-Ca^{2+}Cl^-$ structures are unstable in water. The conflicting properties of wet strength and water-disintegrability may be added to the sheets, in which CMC with heterogeneous chemical structures is retained, by selecting weight ratios of EtOH/H$_2$O/CaCl$_2$ used as the impregnation liquid for wet wiping sheets.

7.5 References

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Chapter 8

Summary

  The mechanism for the carboxymethyl cellulose (CMC)-rich cellulose sheets, that is applied to wet wiper sheets disposable in toilet, to have wet strength in wiping and water-disintegrability in disposing and flushing in toilet bowl, was studied in detail from the analytic point of view, in order to explain scientifically the obtained knowledge and develop the next innovative technology and product items. The influence of chemical structures of anionic polysaccharides except CMC on physical properties of the composite sheets was also studied by characterizing anionic polysaccharides.

Chapter 2

Characteristic data such as DP and charge density, and analytical methods of polymers and cellulose fiber (Softwood bleached kraft pulp) used in sheet-making are described in detail. Characterizations of the materials used in this study, were carried out in order to analyze the composite cellulose sheets prepared with these materials from stoicheiometric view in the following chapters.

Chapters 3

The cellulose sheets were prepared from cellulose slurries with 5% PTMMAC and 5% CMC with DS of 0.96 using a papermaking technique, and approximately 94% of both PTMMAC and CMC added were retained in the sheets, forming carboxylate amine salts between PTMMAC-N$^+$ and CMC-COO$^-$ molecules. When the PTMMAC/CMC/cellulose sheets are soaked in the EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 75:24:1, almost all PTMMAC and CMC molecules remain in the sheets, forming the structures of PTMMAC-N$^+$Cl$^-$ and CMC-COO$^-$Ca^{2+}Cl$^-$. Thus, accurate PTMMAC-N$^+$, CMC-COO$^-$ and Ca^{2+} contents in the soaked and then dried sheets can be calculated from nitrogen, calcium and chlorine contents determined by analytical methods. When the EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 20:79:1 was used in the soaking treatment, sufficient wet tensile strength of 6 Nm g^{-1} appeared on the sheet, probably because of low dissociation degrees of carboxylate groups of the CMC-COO$^-$Ca^{2+}Cl$^-$ structures in the EtOH-containing soaking solutions. On the other hand, no wet strength was observed for the sheets soaked in the EtOH/H$_2$O/CaCl$_2$ solution with the weight ratio of 0:99:1 by sufficient dissociation of the CMC-COO$^-$Ca^{2+}Cl$^-$ structures in water. Thus, the trade-off properties of wet strength

and water-disintegrability can be added to the PTMMAC/CMC/cellulose sheets by selecting weight ratios of EtOH/H$_2$O/CaCl$_2$ used as the impregnation liquid for wet wiping sheets.

Chapter 4

The simple determination methods of PTMMAC and CMC contents in cellulose sheets prepared with these polymers by the dual polymer system were established by calculation from nitrogen and calcium contents in the sheets. The determination method is not only convenient for treating a lot of samples than other methods but also safer for experimenters and environment. These methods are established based on the hypothesis that all CMC molecules retained in the cellulose sheets form the CMC-COO$^-$Ca^{2+}Cl$^-$ structure after the soaking treatment in EtOH/H$_2$O/CaCl$_2$ solution, based on the results by XRFA and SEM-EDX analyses (Chapter 3) and the assumption that calcium and chloride ions are homogeneously distributed in the sheets.

Chapter 5

Relatively large amounts of CMC molecules with DS 0.96 can be retained in the cellulose sheets, when PTMMAC is used as the co-additive in the cationic/anionic dual polymer system. When 5% PTMMAC and 5% CMC are added to the cellulose fiber slurry, PTMMAC-N$^+$ and CMC-COO$^-$ of ~30 mg g^{-1} and 35-38 mg g^{-1}, respectively, are retained in the sheets regardless of DP$_w$ values of PTMMACs. These PTMMAC-N$^+$ and CMC-COO$^-$ contents in the sheets correspond to ~80% and ~90% retention ratios, respectively; CMC molecules can be retained in the sheets quite effectively by the dual polymer system. Because the surface charges of cellulose fibers and colloidal particles in the cellulose slurry with 5% PTMMAC and 5% CMC are almost zero, suitable charge balances between anionic and cationic groups in the cellulose slurry result in such high retention ratios of PTMMAC and CMC in the sheets. The maximum dry tensile strength is obtained for the sheets prepared with 5% PTMMAC and 5% CMC, indicating that the polyion complexes of PTMMAC/CMC electrolytes homogeneously present in the sheets play a role in reinforcing inter-fiber bonds in the sheets. Though the difference in DP$_w$ of PTMMAC between 342 and 6450 has nearly no influence on CMC retention behavior or wet/dry tensile strength, the water-disintegrability of the sheets is significantly affected by the DP$_w$ values of PTMMAC; the lower the DP$_w$, the clear higher the water-disintegrability of the sheets. Thus, suitable conditions to manufacture the PTMMAC/CMC/cellulose sheets for wet wipers can be designed based on the results obtained in this study.

Chapter 6

The influence of DS of CMC on dry and wet-tensile strengths of CMC-rich cellulose sheets prepared by dual polymer system is studied. Though dry-tensile strengths of the sheets have little difference between the sheets with CMCs of different DS values, wet-tensile strengths of the sheets soaked in EtOH/H_2O/$CaCl_2$ solution depend on the DS value of CMC in the sheets. Especially when the composition of soaking solution is water-rich, the DS value of CMC in the sheets is increased, wet-tensile strength of the sheets increases. The obtained results show that the quantity of the CMC-COO$^-$Ca^{2+}Cl$^-$ structure formed between CMC and $CaCl_2$ in the soaking solution contributes to the development of wet-tensile strength of the sheets. Moreover, the formation of such salt structures promotes insolubilization of CMC molecules in EtOH/H_2O/$CaCl_2$ solution. Therefore, the importance of the CMC-COO$^-$Ca^{2+}Cl$^-$ structure on the development of wet-tensile strength of the sheets prepared with CMC and a cationic polymer is established.

Chapter 7

The influence of chemical structure of anionic polysaccharides on wet strength of the cellulose sheets prepared by the dual polymer system is studied. When alginate or cellouronate-containing sheets (ALG or CUA sheets) are soaked in solutions consisting of ethanol, water and calcium chloride (EtOH/H_2O/$CaCl_2$ solution) with the weight ratio of 25:74:1, most of PTMMAC molecules are removed and only ALG or CUA molecules remain in the sheets, forming not only –COO$^-$Ca^{2+}Cl$^-$ structures but also some cross-linked structures such as (–COO$^-$)$_2$Ca^{2+}, different from those of the CMC sheets. The water-disintegrability of ALG or CUA sheets soaked in the EtOH/H_2O/$CaCl_2$ solutions does not appear, unlike CMC sheets. Such differences of physical properties of these sheets and interactions between carboxylate groups of anionic polysaccharides, Ca^{2+}, and Cl$^-$ are probably due to the different distribution of carboxylate groups in the polysaccharides used.

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List of Publications

International journal publications
<Documents of submitted from Graduate School of Agricultural and Life Sciences, The University of Tokyo>

1. Takehiko Uematsu, Yoshiaki Matsui, Shusuke Kakiuchi, Akira Isogai (2011) "Cellulose wet wiper sheets prepared with cationic polymer and carboxymethyl cellulose using a papermaking technique." *Cellulose* **18**, 1129-1138.

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4. Takehiko Uematsu, Masayuki Hirota, Erika Watanabe, Yoshiaki Matsui, Shusuke Kakiuchi, Tsuguyuki Saito, Akira Isogai (2011) "Influence of chemical structures of anionic polysaccharides on wet strength of cellulose sheets prepared by dual polymer system." *Cellulose* to be submitted.

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5. Kunihiro Osaki, Tadashi Inoue, Takehiko Uematsu (2000) "Stress overshoot of polymer solutions at high rates of shear: semidilute polystyrene solutions with and without chain entanglement." *Journal of Polymer Science, Part B: Polymer Physics* **38** (24), 3271–3276.

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Patents

1. <u>植松　武彦</u>、磯貝　明　"アニオン系官能基を有する高分子量物質からなる添加剤の定量方法"、2009 年 5 月、特開 2010-14707／特願 2009-125267
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1. <u>Takehiko Uematsu</u>, Shusuke Kakiuchi, Yoshiaki Matsui, Akira Isogai "Mechanism of wet strength development of handsheets prepared with carboxymethyl cellulose by dual system." *2010 Pan Pacific Conference*, April 2010, Melbourne, Australia (Poster presentation).

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1. <u>植松　武彦</u>、垣内　秀介、松井　芳明、磯貝　明、"カチオン―アニオンデュアルシステム系における添加剤の定着機構と紙物性の関係"、第 75 回紙パルプ研究発表会、2008 年 6 月、東京都・タワーホール船堀

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1. 植松　武彦、垣内　秀介、松井　芳明、磯貝　明、"デュアルシステムによってカルボキシメチルセルロースを定着させた紙の特性解析"、第 75 回紙パルプ研究発表会、2008 年 6 月、東京都・タワーホール船堀

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Acknowledgement

This thesis is based on the study which has been carried out under the direction of Professor Akira Isogai, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, from 2007 to 2012.

The author wishes to express his sincere gratitude to Professor Akira Isogai, for his continual guidance, advice, instructive discussion and encouragement throughout the course of this work.

The author also wishes to express extraordinary Professor Minoru Kimura, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, for his helpful and valuable discussions and comments during this study.

The author also wishes to express Associate Professor Toshiharu Enomae, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, for his helpful and valuable discussions and comments during this study. He advised how to use the handsheet-making machine and energy dispersive X-ray scanning apparatus equipped in electron scanning microscope (SEM-EDX).

The author also wishes to express Assistant Professor Tsuguyuki Saito, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, for his helpful and valuable discussions and comments during this study. He also supported me by advising how to operate X-ray fluorescence analysis (XRFA) instrument, colloidal titration apparatus, UV-vis light transmittance measurement instrument, and optical microscope.

The author also wishes to express Assistant Professor Miyuki Takeuchi, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, for her helpful and valuable discussions and comments during this study.

The author also wishes to express Professor Takayuki Okayama, United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, for his valuable comments and detailed criticisms on the manuscript of this thesis.

The author also wishes to express Associate Professor Tadahisa Iwata, Department of Biomaterials Sciences Graduate School of Agricultural and Life Sciences, The University of Tokyo, for his valuable comments and detailed criticisms on the manuscript of this thesis.

Special thanks are also due to Dr. Shigeru Tamura, Mr. Masaki Tsumadori, Mr. Shusuke Kakiuchi, Mr. Motomitsu Hasumi, and Mr. Akihito Shizuno, Global Research