

# Hydrogen Bonding Formation and Physicochemical Properties of Chemically Modified Cellulose

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## 論 文 内 容 の 要 旨

Properly modified cellulose derivatives have chemical stability and biodegradability as does the natural cellulose, and increasing attention has been paid to the cellulose derivatives as substitutes for the synthetic polymers, because they have potential to be endowed with new physicochemical properties by modification with various functional groups. Recently developed method to prepare regioselectively substituted cellulose derivatives is expected to be applied to produce the ecological materials for the next generation. However, facile methods to characterize cellulose derivatives are lacking, and the relationship between the physical properties and the formation of hydrogen bonds of the derivatives is not clarified. This probably is the main reason why only a few kinds of cellulose derivatives have commercial values.

This thesis is focused on three aims. The first aim is to establish a facile method to determine the distribution of the substituents in regioselectively substituted *O*-methylcellulose (2,3MC-*n*: *n* = 1-3). The second concerns with the effect of the formation of hydrogen bonds on gelation of 2,3MC-*n* and commercially available *O*-methylcellulose (R-MC) in two-components solvent systems. The third is the preparation of two kinds of cotton fabrics by randomly and low degree substitution of functional groups which have potential to widen application of cellulose derivatives.

Chapter 2 is devoted to the establishment of a new convenient method to determine the distribution of methyl groups in 2,3MC-n on anhydroglucose unit using solution  $^1\text{H-NMR}$  analysis. The determination was based on the assignment of the signals of each proton, which directly attached to the glucopyranose ring carbon for 2,3MC-n samples observed in  $\text{D}_2\text{O}$ . The results of the new method were in agreement with those based on the gas-chromatographic analysis. This method can also be applied to the measurements of the distribution of methyl groups for R-MC.

Chapter 3 describes the effect of the formation of hydrogen bonds and the distribution of methyl groups on gelation using 2,3MC-n and R-MC. 2,3MC-n and R-MC behaved differently in forming gel and the DSC thermograms on heating. The formation of hydrogen bonds with each water molecule in the sample solution has been revealed by the curve fitting of OH stretching region of water molecules in the near IR spectra, which were composed of water species S0, S1, and S2. The presence of intermolecular hydrogen bonds between samples and water molecule was observed. The gelation of *O*-methylcellulose was attributed to the hydrophobic interactions and also to the hydrogen bonds which depended on the amount of hydroxyl groups at C(6) position.

Chapter 4 describes the effect of dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ )/water composition on gelation behavior of 2,3MC-n and R-MC investigated by NIR. All the 2,3MC-n series and R-MC samples were observed that the gelation occurred at room temperature in  $\text{Me}_2\text{SO}/\text{water}$  (70/30 (wt/wt%)) system, while all the samples remained as a sol in  $\text{Me}_2\text{SO}$ . On the other hand, some of them showed a gelation upon heating in water. These gelation behaviors can be correlated to the change in the areas of S0, S1 and S2 of OH band in the solutions. When  $\text{Me}_2\text{SO}/\text{water}$  composition was between 90/10 and 80/20,  $\text{Me}_2\text{SO}$  interacts poorly with  $\text{Me}_2\text{SO}$  or water, this suggests the presence of intermolecular hydrogen bonds between the samples and water. The strong interaction between  $\text{Me}_2\text{SO}$  and water molecules causes the reduction of the interaction of the sample with either  $\text{Me}_2\text{SO}$  or water when  $\text{Me}_2\text{SO}/\text{water}$  composition was between 70/30 and 50/50.

In Chapter 5, the preparation of three kinds of water-repellent cotton fabrics, A, B, and C, is described. Sample A was prepared by alkylation through acetylation without mercerization, Sample B, by direct alkylation after mercerization, and Sample C, by alkylation by means of allylation and bromination. Water repellency of the treated samples was similar to that of cotton fabric treated with Scotch-Gard<sup>®</sup>, however water repellency of the samples did not fade out through twenty launderings in contrast to that treated with Scotch-Gard<sup>®</sup>. Durability of water-repellency after repeated launderings depended on the fabric construction. These samples retained a fabric hand, water-vapor permeability, and biodegradability similar to those of untreated cellulose fabric.

Chapter 6 is described successful preparation of durable flame retardant cotton fabric by partial orthophosphorylation and pyrophosphorylation, followed by metal-complexation. Metal content, the residue after thermal degradation, and flame retardancy depended on total phosphorus content. Pyrophosphorylated cotton fabric treated with  $\text{Ni}^{2+}$  had an LOI (limited oxygen index) value of 28, which was comparable to that obtained by the resin finishes of cotton fabric with an organophosphorus compound. Flame retardment, tensile strength and elongation of the treated fabrics did not decrease after launderings. The pyrophosphorylated sample

had a tensile strength, elongation, fabric hand and biodegradability similar to those of untreated fabrics.

In Chapter 7, conclusions of this study are briefly summarized. Future directions for the study are also indicated.

The results presented in this thesis will open new application in the field of cellulose science and industry, as well as in the other fields of polysaccharide sciences.

## 論文審査結果の要旨

天然セルロースを化学修飾したセルロース誘導体は、官能基の種類によって様々な性質の付与が可能のため、合成高分子の代替材料のみならず、環境への負荷が小さい新規機能材料として期待されている。本論文では、セルロース産業技術に必要な3つの目的が掲げられた。第1は位置選択置換メチルセルロースにおける簡便な置換度測定法の確立、第2はメチルセルロースのゲル化における置換基分布と水素結合様式の影響の解明、第3は低置換誘導体化を利用したセルロース繊維集合体への化学修飾である。

第1章では、セルロース系材料とその化学における現状と課題を概観し、研究の目的と位置づけが詳述されている。

第2章では、 $^1\text{H-NMR}$  測定による、位置選択置換メチルセルロースの置換基分布測定法を新規に確立している。この方法は、現在行われている $^{13}\text{C-NMR}$  法やGC法による方法に比べて測定時間の短縮化と分析ステップの簡略化、および必要サンプルの少量化を可能とし、さらに市販のランダム置換メチルセルロースにも有効であることが示唆された。

第3章では、異なる置換度をもつ位置選択置換メチルセルロースと、市販のランダム置換メチルセルロースの水溶液のゲル化挙動をDSCおよびFTIRによって検討することにより、メチルセルロースのゲル形成機構を解明している。ゲルおよびゾル状態でのFTIRの近赤外線領域における水のOHバンドを波形分離し、水分子の3種類の水素結合様式を解析することにより、メチルセルロースのゲル化において、6位のOH基と水との分子間水素結合が関与していることが証明された。

第4章では、異なる混合比のジメチルスルホキシド/水の混合溶媒中で、選択置換メチルセルロースと市販のランダム置換メチルセルロースのゲル化挙動を検討することにより、溶媒とメチルセルロースとの相互作用性の観点からゲル形成機構を解明している。

第5章および第6章は、繊維集合体レベルでの化学修飾について応用を試みたものである。置換度を極度に低くおさえることにより、木綿布の強度、生分解性、風合いの保持を可能にしながら、第5章では長鎖アルキル基によって化学修飾し、耐洗濯性の高撥水綿布を得ており、また第6章では、ピロリン酸基を置換後の金属錯体形成により、難燃化綿布が得られることを示している。

第7章は結論であり、本論文の研究内容をまとめ、今後の課題と展望が述べられている。

以上のように本論文は、セルロース化学および産業に有用な新たな知見を提案しており、博士(工学)の学位を授与するに十分な内容を持つものと認定する。