

New Aqueous Dispersion of Cellulose Sub-micron Particles: Preparation and Properties of Transparent Cellulose HydroGel(*TCG*)

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New cellulosic material, Transparent Cellulose HydroGel(*TCG*), was prepared through the two processes; the hydrolysis reaction of the regenerated cellulose obtained from the Cellulose-65wt% aq. sulfuric acid dope/water coagulation system and the finely smashing by using a Microfluidizer™ (Mizuho Kogyo Co.,Ltd). *TCG* was composed of water and the cellulose microfibriles with ca.0.2 μ m size and low crystallinity. Furthermore, the particles in *TCG* have a negative charge based on a cellulose surface, influencing unique rheological properties of *TCG* and its diluted suspension. The strong association ability and the affinity for various hydrophilic compounds, which the particles in *TCG* have, will make various applications as an additive in the wide industrial fields.

Key words: Cellulose, Hydrogel, Hydrolysis, Transparent, Sub-micron particles, Rheology

1. INTRODUCTION

Many attempts have been undertaken in order to obtain the functional materials by a cellulose resource, resulting in many cellulosic productions roughly in the two categories. The first group is the pure cellulose products like as fiber, dialysis membrane, sponge and powder, obtained by regeneration, hydrolysis, or mechanical treatment. The another category is the chemical substituted products such as the cellulose derivatives and the reinforced cellulose by crosslinking technique. The cellulose derivatives have been widely used as water-soluble additive, plastic and hydrophobic coating material and so on, but have lost a character as "raw material".

Considering the recent abrupt demand for a raw material, attempts to find a new functional cellulosic material within the restriction of no chemical substitution of cellulose backbone might be attractive theme. We had been carrying out the many trials in this view, then succeeded in obtaining the unique hydrogel [1] composed of water and cellulose particles with a sub-micron size, which had high transparency and extraordinary high viscosity as compared with the conventional cellulose suspensions (e.g. microcrystalline cellulose (*MCC*) [2] and microfibrillated cellulose (*MFC*) [3]).

As far as the suspension of cellulose sub-micron particles is concerned, the aqueous suspension of whiskerlike microfibriles (cellulose whisker) was only reported [4,5]. This suspension has been especially noticed on the property forming chiral nematic phase [6]. In the articles, the anisotropic optical character bases both on the rod-like shape (whisker) and on high negative charge of the particle surface by inducing the sulfate group because of the severe hydrolysis condition (using 55wt%–65wt% aqueous solution of sulfuric acid at above 60°C). For this, the suspension of cellulose whisker cannot be regarded as a pure cellulose product, and in addition, have a disadvantage as an industrial

manufacturing process because it needs the severe purification process such as dialysis.

The new material, transparent cellulose hydrogel, hereafter referred to as *TCG*, can be prepared through industrially realizable process because the purification can be carried out relatively easily [1]. Various unique properties of *TCG* will enable this new material to be utilized in the wide industrial fields. In this report, we introduce the preparation, characterization and some properties of *TCG*.

2. EXPERIMENTAL

Preparation of *TCG*

210 grams of cellulose dope with 4.76 wt% of cellulose concentration were prepared by dissolution of dissolving pulp (D.P. \approx 1,100) into 65wt% aqueous sulfuric acid at 0°C. The dope was poured into 480 g of water under the stirring at 3000 rpm by using T.K.Robo.mics (Tokusyu Kika Kogyo. Co.,Ltd., Japan) to precipitate the flock-like cellulose solid having ca. 0.5 mm in size. This suspension of cellulose, in which the dispersing medium was aqueous sulfuric acid with acid concentration of 19.1 wt%, was continuously heated to 80°C, then kept this temperature for 20 minutes (hydrolysis process). The suspension after the hydrolysis treatment was poured into G-4 type's glass filter under vacuum by using an aspirator. Note that the suspension has not changed at first glance before and after the hydrolysis, and that the dispersing medium (aqueous sulfuric acid) easily passed through the filter. Obtained

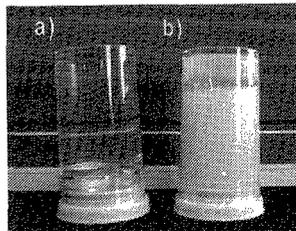


Fig.1 Samples *TCG*-2.0 (a) and *MCC*-2.0 (b); both have 2wt% solid fraction and are composed by the particles with ca. 0.2 μ m size.

white flocks were washed with large amount of deionized water repeatedly, and gradually became paste-like state. When pH value of the paste becomes above ca. 3, the paste was washed with very dilute aqueous solution of NH_3 , and washed again with deionized water. By the above procedures, white translucent suspension of cellulose in paste state with pH = 6 (having a solid fraction of 5.5wt%) was obtained (*Pre-TCG*).

Pre-TCG was diluted to a solid fraction of 2wt% by deionized water, and the diluted suspension was premixed by using a homomixer, T. K. Lobo micsTM (Tokusyu Kika Kogyo Co.,Ltd., Japan) under the 10,000 rpm for 10 minutes. The slightly viscous suspension obtained (*Pre-TCG-2.0*) was smashed by using a MicrofluidizerTM M-110EH (Mizuho Kogyo Co.,Ltd., Japan). The smashing condition was as follows; pressure: 1750 Kg/cm², passing times through the machine: five times. While smashing was proceeded, the viscosity of the fluid gradually became higher, and finally became a transparent gelatinous gel (Fig.1a). The transparent hydrogel obtained was referred to as *TCG-2.0*. As a reference, aqueous *MCC* suspension having 4.4 μm in a weight-averaged particle size, R_w , was prepared by obeying the previous method [7] and the 2wt% *MCC* suspension was smashed by a Microfluidizer under the above smashing conditions. Finally the slightly white suspension not in gel state was obtained (sample *MCC-2.0* (pH=7), Fig.1b).

3.RESULTS AND DISCUSSION

3.1 Characterization

By drying the *TCG-2.0* sample, transparent resin-like solid (dried *TCG*) was obtained. As a result of the investigation of solubility, it was confirmed that this solid was only soluble in the convenient solvents for cellulose. ¹³C NMR spectrum of the 7wt% solution of the dried *TCG* in which solvent was a mixture of LiCl/DMAc/DMSO-d₆ (9/64/27(g/g/g)) led us to the conclusion that the constituent particles of *TCG* is composed by nearly pure cellulose, at least, in the bulk level. Additional work on the evaluation of spin-spin relaxation time, T_2 , of *TCG* sample by means of a pulse NMR spectrometer, JNM-Mu25 (JEOL Co.,Ltd, Japan), showed that the relaxation curve contained a certain Gaussian component having T_2 value in the order of μs , indicating the existence of the component in glassy state (cellulose solid, not dissolving).

As a result of the intrinsic viscosity measurements for the dried *TCG-2.0* / cadoxen solution at 25°C, the degree of polymerization of the dried *TCG-2.0* sample was evaluated to ca. 40 by obeying the incited parameters [8] of Mark-Houwink-Sakurada equation for cellulose/cadoxene solution. This corresponds to the value of leveling-off degree of polymerization (LODP) of regenerated cellulose [9].

In order to discuss the surface property of the particles, the zeta potential of particles was estimated. Because it was well-known that the cellulose whisker, which is prepared through the hydrolysis reaction in the concentrated aqueous solution of sulfuric acid, has the sulfate ester group in a particle surface.

The results of zeta potential measurements by using an electro-phoretic light scattering analyzer, ELS-800 (Otsuka Electronics, Japan) for the three suspension

Table I Zeta(ζ) potentials of three cellulosic suspensions at 25°C

Sample	ζ potential (mV)
Dilute suspension of <i>TCG-2.0</i>	-30
Dilute suspension of <i>MCC-2.0</i>	-32
Suspension of cellulose whisker ^a	-84

a, preparation method: ref.6.

samples, the dilute suspensions of *TCG-2.0* and *MCC-2.0*, and the aqueous suspension of cellulose whisker (pH=6) prepared by obeying the previous article [6], are summarized in Table I. Note that all dilute suspensions were preliminarily dialyzed repeatedly. The absolute value of zeta potential for the dilute suspension of *TCG* was significantly smaller than that for the suspension of cellulose whisker, and as nearly same as that for *MCC* suspension. The zeta potentials of cellulose materials were almost reported within the range of -40mV to -20mV [10]. Those results suggest that the sulfate groups were not introduced to a particle surface essentially in the preparation process of *TCG*.

Summarizing, the particles constituting *TCG* can be regarded as almost pure cellulose although having low molecular weight (ca. $6 \times 10^3 - 7 \times 10^3$).

3.2 Shape and size of particles constituting *TCG*

The shape and the size of the particles constituting *TCG* should intimately affect the gel or suspension properties of *TCG*, e.g., rheological properties.

Fig.2a and 2b show the images of the scanning probe microscopy (SPM) with the different scales observed for the as-cast surface on slide glass of the highly diluted suspension by water against *TCG* (cellulose concentration: below 0.002wt%), which were measured by tapping mode by using a Nano Scope IIIa (Digital Instruments Corporation, USA). Glancing at Fig.2a leads us to the conclusion that *TCG* is constituted by the fibril-like particles (microfibriles), and that each particle vigorously associates each other. Fig.2b, the image closed up to Fig.2a, proposes that the microfibriles are furthermore made by the primary spherical particles with a radius of 10–15 nm in series (shown by white circles in the figure, the width of the fiber: ca. 10–15 nm). The spherical particles found in the figure will

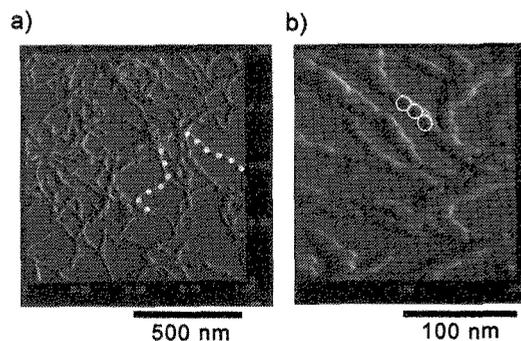


Fig.2 SPM images with different scales of the as-cast residue on a glass plate from the dilute suspension of *TCG-2.0*. The dotted line in Fig.2a and circle in Fig.2b reveal the image of single microfibril and a primary particle constituting a microfibril, respectively.

belong to the primary spheres (with 10–30 nm in size) observed widely for the SPM image of the other regenerated cellulose materials [11].

In addition, any independent primary spheres cannot be found in the figures, suggesting that the fundamental particles constituting *TCG* is not a sphere but a microfibrile. This speculation is also supported by the results of the estimation of particle size discussed below. The primary spherical particles should be linked in series in one microfibrile by a stronger bond than a hydrogen bond, i.e., a covalent bond, through tie molecules. Under the more severe hydrolysis condition than that in the *TCG* preparation process, the independent spherical particles with ca. 10-15 nm probably will be obtained [12].

The particle size distribution was evaluated by a particle size analyzer by laser scattering method, LA-920 (Horiba Corporation, Japan) at room temperature. Here, the particle size corresponds to a sphere corresponding diameter calculated using Mie's scattering theory [13].

Fig.3 shows the particle size distributions of *MCC-2.0* sample. In the measurements, the ultra-sonic treatment for 10 seconds was performed on the sample stepwisely. The distribution under no ultrasonic treatment locates over 10 μ m in size, indicating that only the domain formed by the associating particles was recognized in a distribution. With increasing the steps of ultrasonic treatment, the distribution profile became bimodal in which the larger distribution shifts to the smaller size with performing the ultrasonic treatments and the smaller one locating below 1 μ m did not change its position and became larger in the intensity. Finally the distribution below 1 μ m almost only was observed. The weight average particle size, R_w , of the distribution below 1 μ m was calculated to 0.16 μ m. The R_w value is interpreted as nearly a size distribution of fundamental particles (microfibriles) of *TCG*.

In contrast to this, the same measurements for *MCC-2.0* revealed that any distribution for associating particles was not observed and only the distribution below 1 μ m was recognized even under no ultrasonic treatment. The R_w value was 0.12 μ m.

The results on the size distribution of the *TCG* and *MCC* samples suggests that the strength of association of

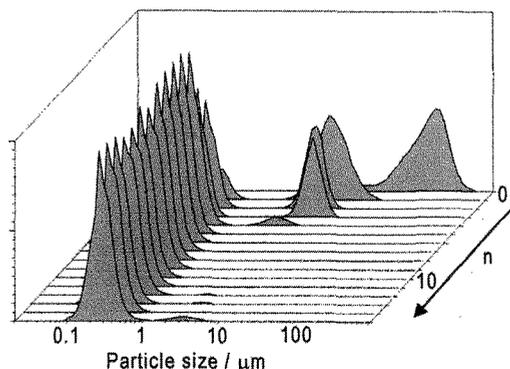


Fig.3 Particle size distributions of sample *TCG-2.0* by using a laser scattering method. n means the number of steps of ultrasonic treatment for 10s.

the particles in *TCG-2.0* is significantly larger than that in *MCC-2.0*. The fundamental particles of *MCC* suspension have rigid rod-like shape [7] in contrast to the fibrile-like shape of those for *TCG*. The effective density of association which the cellulose particles can be formed per volume might relate both the size and the shape.

In addition, we confirmed that the dried *TCG* have very low crystallinity as compared with relatively high crystallinity of *MCC*. by means of wide-angle X ray diffractions. The crystal forms of two samples were also different; the dried *TCG*, cellulose II form; *MCC*, cellulose I form. The difference on such a microscopic standpoint will probably also affect the feature of *TCG*, i.e., the above strong association between the particles and the high transparency.

3.3 Properties

Structural features of the particles in *TCG*, discussed above, produce some unique properties which any other cellulosic aqueous suspension does not have. In this report, summaries of them are introduced.

Fig.4a and 4b give the Shear stress, τ (a) and shear

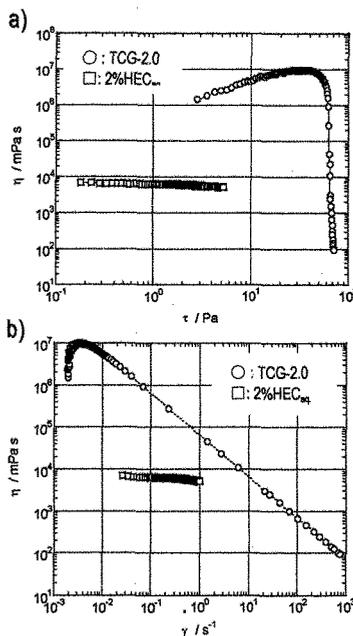


Fig.4 Shear stress, τ (a) and shear rate, γ (b) dependences of the viscosity η estimated for *TCG-2.0* and 2wt% aqueous hydroxyethylcellulose (*HEC*) solution at 25°C.

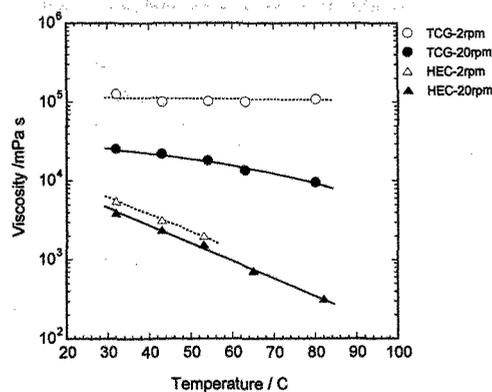


Fig.5 Temperature dependences of the viscosity under the two different revolution numbers on a B-type viscometer estimated for *TCG-2.0* and 2wt% aqueous *HEC* solution.

rate, γ (b) dependences of the viscosity, η , respectively, estimated for TCG-2.0 and 2wt% aqueous hydroxyethylcellulose (HEC) solution at 25°C. Viscosity of the HEC solution does not depend on τ and not on γ , indicating a typical Newtonian fluid. In contrast to this, the curve of η versus τ and the curve of η versus γ for TCG sample show that the viscosity decreases abruptly in the range above a critical shear stress revealing the collapse of the network structure at that shear stress, and that the monotonous decrease of η with increasing the γ value suggesting the typical thixotropic property, respectively. The rheological properties of TCG was supported by a network formed by cellulose microfibrils having sub-micron size [1].

Fig.5 shows the temperature dependence of the viscosity under 2rpm and 20rpm observed for TCG-2.0 and 2wt% aqueous HEC solution by using a B-type viscometer, model BH (Tokimec INC, Japan). Under both revolution numbers, the viscosity of HEC solution decreases with increasing temperature similar to many other aqueous solutions or suspensions. It was, however, found that the viscosity of TCG-2.0 under low shear stress (2rpm) shows almost a constant in the range of ca. 30°C–80°C. Under relatively high shear stress (20rpm), a gradual decreasing of the viscosity was observed for TCG-2.0 with an increase in temperature. The network structure in TCG might be stable in the wide range of the temperature under the static state. However, under the high shear stress, the temperature dependence of the viscosity of TCG approaches to that of the convenient aqueous polymer solution because of the collapse of network.

The above discussions were primarily poured into a homogeneous interaction for cellulose microfibrils. The second feature of TCG is pointed out for a

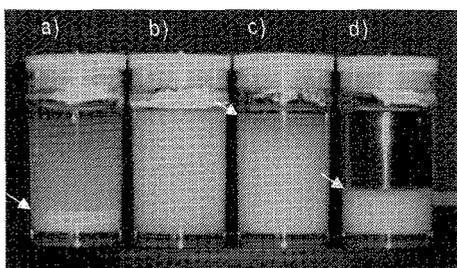
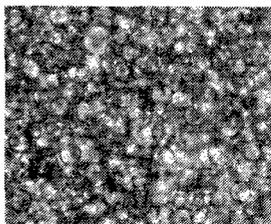


Fig.6 Additive effect of the sedimentation of SiO₂ particles/H₂O=10/90(g/g) suspensions with pH \approx 7(SiO₂ particles having ca. 3.7 μ m size); a) no additive, b) addition of 0.5wt% cellulose supplied by TCG-2.0, c) addition of 0.5wt% HEC, d) addition of 0.5wt% Na-carboxymethylcellulose (CMC-Na). The photographs show the samples which had been left for 10 days after the mixing treatments (arrows: the position of the sedimentation layer of SiO₂).



50 μ m

Fig.7 Optical micrograph of the emulsified dispersion from the mixture of liq. paraffin/cellulose/water(40/1/59 (g/g/g)), in which cellulose had been supplied by TCG-2.0. R_w of oily particles was ca 10 μ m.

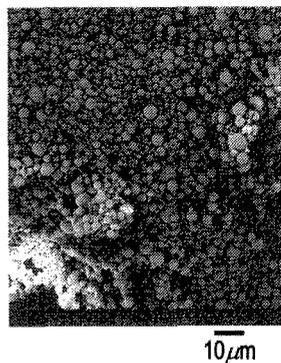


Fig.8 SEM micrograph of the cellulose microsphere prepared from TCG-2.0 by the spray drying method ($R_w = 3.3\mu$ m).

heterogeneous interaction between a cellulose microfibril and other compound, especially inorganic particles such as SiO₂ and TiO₂, and oily compounds, in aqueous media. The small and flexible TCG particles easily interact with multiple kinds of chemical species, resulting in a stabilization of the heterogeneous aqueous suspension. The examples applied to the dispersions of SiO₂ particles and liquid paraffin are given in Fig.6 and Fig.7, respectively.

It was found that, by drying of the coating layer of TCG on the glass plate or plastic films, transparent and relatively hard membrane was formed.

Furthermore, it was found that drying of TCG by means of a spray drying method gave the cellulose microsphere having from 1 μ m to 4 μ m in average diameter (Fig.8). This is a new route of preparation of cellulose microsphere. Any stable preparation method to supply a cellulose microsphere with those micro sizes have never been reported.

Thus, TCG and the TCG derived materials will be expected to expand the applications of cellulose in the wide range of industries.

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