

Preparation and Properties of Chemical Cellulose from Ascidian Tunic and Their Regenerated Cellulose Fibers

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ABSTRACT: Chemical cellulose (dissolving pulp) was prepared from ascidian tunic by modified paper-pulp process (prehydrolysis with acidic aqueous solution of H_2SO_4 , digestion with alkali aqueous solution of $NaOH/Na_2S$, bleaching with aqueous $NaOCl$ solution, and washing with acetone/water). The α -cellulose content and the degree of polymerization (DPw) of the chemical cellulose was about 98 wt % and 918, respectively. The Japanese Industrial Standard (JIS) whiteness of the chemical cellulose was about 98%. From the X-ray diffraction patterns and ^{13}C -NMR spectrum, it was found that the chemical cellulose obtained here has cellulose I β crystal structure. A new regenerated cellulose fiber was prepared from the chemical cellulose by dry-wet spinning using *N*-methylmorpholine-*N*-oxide (NMMO)/water (87/13 wt %) as solvent. The new regenerated cellulose fiber prepared in this study has a higher ratio of wet-to-dry strength (<0.97) than commercially regenerated cellulose fibers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1634–1643, 2002

Key words: ascidian tunic; chemical cellulose; NMMO; α -cellulose

INTRODUCTION

Pulp is the fibrous material separated from wood or other plant fiber materials. Although softwood, temperate hardwood, and some selected species of tropical hardwood constitute the major bulk of the world pulp and papermaking material and this is true where wood is plentiful and thus relatively cheap, in many areas of the world, wood resources are now limited. So, nonwood plant fibers are a potential source of raw material in many countries where pulpwood supplies are limited or nonexistent. Bagasse, bamboo, cereal straw, and reeds are the dominant raw materials among the nonwood fibers for the production of

pulp and a wide range of papers and boards.¹ Also, tunicate in protochordata (an ascidian, a sea squirt; *Cynthia roretzi*), a kind of sea animal, produces highly crystalline cellulose I. In Korea, there are a good deal of cultured ascidian tunicates. The ascidian tunic is a waste material and the discharging of ascidian tunic into the sea has been blamed for problems of coastal environmental pollution.

Pulping is achieved by chemical or mechanical means or a combination of the two to extract an α -cellulose-rich product. Cellulose is generally associated with other substances such as lignin and hemicellulose. Pulp has as its purpose the selective removal of the fiber-bonding lignin to a varying degree with a minimum content of the hemicellulose. Hemicellulose acts as a matrix for the cellulose and as a link between the fiber cellulose and armorphose lignin.² Lignin, a polyphenolic compound, acts as a cementing material for wood fibers.^{3,4}

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The properties of the end products will depend on the properties of the pulps used in their manufacture. The sulfate or kraft process was the last invented (1897) of the strictly chemical pulping processes; the soda process, the first chemical process, is no longer included in the statistics of the industry. Delignification of wood was usually performed as a multistep process for more than a century, dissolving the lignin and the hemicellulose via a combined chemical transformation and cleavage and leaving the cellulose component as a solid in a somewhat degraded state. The whole process comprises a so-called digestion, removing most of the lignin as a sulfite process⁵ or as an alkali,⁶ and subsequent bleaching steps⁷ for eliminating nearly all of the residual lignin.

The α -cellulose content of paper pulp was about 78%; however, the α -cellulose content of chemical cellulose (dissolving pulp) was in the range of 90 to 98%. Generally, dissolving grade pulp is produced by modified sulfite and kraft processes. Prehydrolysis-kraft process followed by further purification is a kind of modified kraft process. Prehydrolysis can be carried out in acidic steam or water medium. Further purification for the production of chemical cellulose with higher α -cellulose content may be carried out in the bleaching step. The steam or water prehydrolysis-kraft process followed by multistage bleaching gives an average yield of 32%.

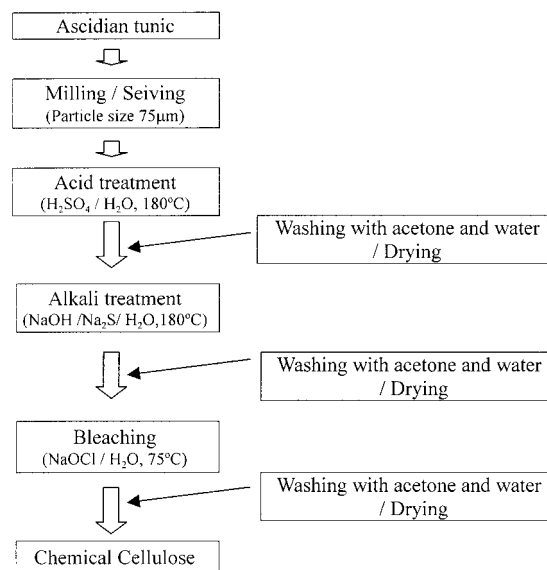
Among all the investigated systems that were reviewed recently,⁸ tertiary amine oxides stand out as very powerful cellulose solvents with great potential either for industrial development⁹ or research.¹⁰ *N*-methylmorpholine-*N*-oxide (NMMO) appears to be the tertiary amine oxide most commonly used to dissolve cellulose.

In this study, chemical cellulose was prepared from ascidian tunic cultured in Korea by the prehydrolysis-kraft process, followed by further purification. The composition, α -cellulose content, structure, and yield with treatment conditions were investigated. A new regenerated cellulose fiber was prepared from the chemical cellulose by using NMMO/water (87/13 wt %) as a solvent by dry-wet spinning. The property of the fiber was investigated.

EXPERIMENTAL

Materials

Ascidian tunic was obtained from a Korean fish market. Reagent grade acetone, sodium hydrox-



Scheme 1 Pulping process (purification process) of ascidian tunic.

ide, sulfuric acid, sodium sulfide (Na_2S), and sodium hypochlorite (NaOCl) were used without further purification. NMMO/water (87/13)^{3,4} was prepared from NMMO/water (50/50) (Aldrich) by vacuum drying. The melting temperature of NMMO/ H_2O (87/13) is 74°C. Chemical cellulose (degree of polymerization, DPw: about 918; Japanese Industrial Study (JIS) whiteness: 918) obtained from ascidian tunic was used to prepare a new regenerated cellulose fiber in this study.

Pulping Process

The starting material was ascidian tunic with its root removed. The dried ascidian tunic was reduced to powder by using a knife mill. The size of ascidian tunic powder used in the pulping process was $< 75 \mu\text{m}$. The pulping process is presented in Scheme 1. The ratio of all treating solutions : pulp was 10 : 1. The 100 g ascidian tunic powder was dipped in the acidic aqueous solution of H_2SO_4 (0.9 wt %) in a stainless steel vessel equipped with a thermosensor, stirrer, and heat jacket, heated to 180°C, and then treated for 2 h under gentle stirring. Then, the ascidian tunic was filtered by using a glass filter, washed with acetone/water, and dried under vacuum at 75°C. The yield of this step was 81%. For the next step, the acid-treated sample was treated with alkali aqueous solution of $\text{NaOH}/\text{Na}_2\text{S}$ (9/3 wt %) for 2 h at 180°C, and also filtered, washed, and dried the same as the process above. The yield of second

Table I Sample Designation, Treatment Conditions, and the Yield of Chemical Cellulose

Sample Designation	Acid Treatment Time (h)	Alkali Treatment Time (h)	Bleaching Time (h)	Yield (%)
W-0	—	—	—	100
W-1	2	—	—	81
W-2	2	2	—	33
W-3	2	2	1	32

step was 33%. Finally, the alkali-treated sample was treated with aqueous NaOCl solution (2.9 wt %) as a bleaching agent for 1 h at 75°C, and then also filtered, washed, and dried in the same process. The final yield was about 32%. The sample designation, treatment conditions, and yield are shown in Table I.

Preparation of Spinning Dope

The mixture of pulp (6 g)/NMMO/water (87/13 wt %, 94 g) containing 0.5 wt % of *n*-propyl gallate to pulp was agitated for 40 min at 120°C and then degassed under vacuum to reach the clear solution to be used as spinning dope.

Spinning

Regenerated cellulose fibers were prepared by dry-wet spinning by using a pressure-type spinning apparatus equipped with a pressure gauge and temperature and spinning controllers. The spinning dope was extruded into a nozzle (one hole, diameter: 0.5 mm, length/diameter: 10) with a pressure of 1.5 kgf/cm² at 110°C. The air gap was 10 cm, and spinning speed was 20–100

m/min. The coagulation bath contains water in 30°C. The regenerated cellulose fibers obtained in this study were washed with flowing water and dried.

Characterization

An elemental analyzer (Profile HV-3, Germany) was used to analyze the elements of samples. The contents of α -cellulose, β -cellulose, and hemicellulose were calculated from residue percentage in 10% NaOH aqueous solution (R10), and soluble percentages S10 and S18 in 10 and 18% NaOH aqueous solutions, respectively, according to ASTM D1696-61. The DP_w was determined from the Mark-Houwink-Sakurada equation by using Ubbelohde viscometer with 1M Cuene (Cupriethylene diamine hydroxide) solution as a solvent (ASTM D1795-62). DP_w of chemical cellulose dissolved in Cuene solution was determined from $[\eta]$ as follows: DP_w = $[\eta] \times 190$, where $[\eta] = \eta_{sp}/c$, $\eta_{sp} = \eta_{rel} - 1$, $\eta_{rel} = t/t_0$, t = time (s) of flow through a viscometer for pulp cellulose solution [$c = 0.1$ g/dL, solvent = 0.5M Cuene solution, and t_0 = time (s) of flow for 0.5M Cuene solution]. The DP_w of the chemical cellulose prepared in this

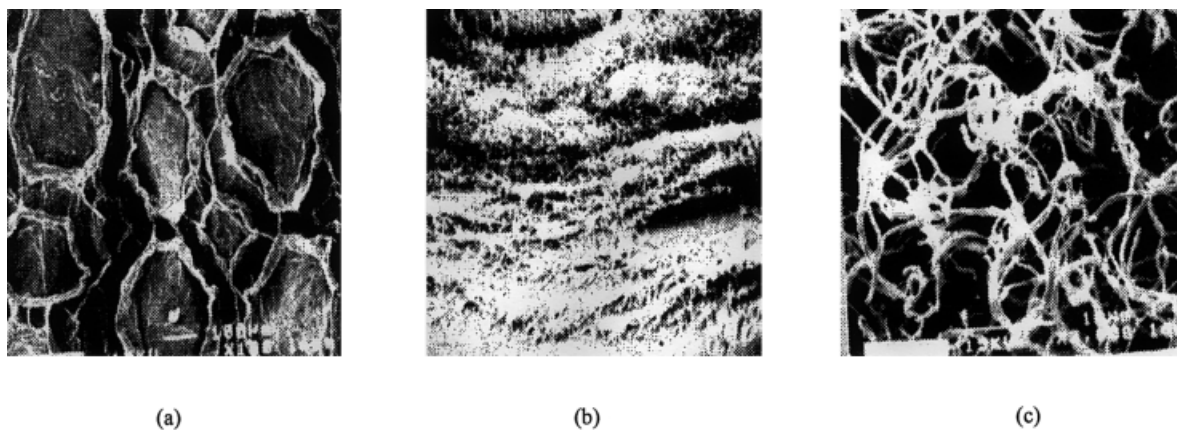


Figure 1 Scanning electron microphotographs of ascidian tunic with magnifications: (a) $\times 100$, (b) $\times 300$, and (c) $\times 3000$.

Table II Compositions of Chemical Cellulose Samples Obtained from Ascidian Tunic and Commercial Pulp V60

	Elements											Whiteness (JIS/ASTM)				
	C	H	O	S	N	Si	Na	Fe	Ca	Cr	Cu (ppm)		Mn	α -Cellulose ^a	β -Cellulose ^b	Hemicellulose ^c
W-0	41.0	6.25	41.7	3.58	6.16	0.22	0.35	0.07	0.65	14.5	42.5	45.4	79.1	13.3	7.6	60/24
W-1	43.1	6.05	44.5	0.00	5.92	0.20	0.21	0.05	0.05	14.2	12.6	0.0	78.6	14.0	7.4	71/40
W-2	42.8	5.99	51.0	0.00	0.00	0.02	0.18	0.03	0.05	3.13	12.0	0.0	96.6	3.0	0.4	90/80
W-3	42.6	6.02	51.3	0.00	0.00	0.01	0.15	0.02	0.05	0.13	4.5	0.0	97.1	2.9	0.0	98/94
V60 ^d	41.9	6.15	51.0	trace	trace	0.12	0.18	0.01	0.05	0.00	2.8	0.0	92.0	8.0	0.0	97/93

^a α -cellulose = R10 + 1/2 (S10 - S18).^b β -cellulose = S10 - S18.^c hemicellulose = 100 - (α -cellulose + β -cellulose).^d V60 commercial pulp from the Buckeye Cellulose Co.

study was about 918. Whiteness was determined from TAPPI 452 om-83 method using UV-visible spectrometer (Shimadzu, PC-1601, Japan). Lignin was analyzed using UV-visible spectrometer (Shimadzu, PC-1601). Optical textures of the cellulose solution were examined by using an Olympus BH2 polarized microscope equipped with a Mettler FP84 hot stage. X-ray diffractometer (Rigaku D/MAX-2400) was used to determine the structure of the chemical cellulose powder. Solid-state ¹³C-NMR (Varian Unity 300 Mz) and FTIR (Nicolet, Impact 400D) spectrometers were used to identify the structure of native ascidian tunic and chemical cellulose. For each IR spectrometer sample, 32 scans at 2 cm⁻¹ resolution were collected in the transmittance mode. Tensile properties of regenerated cellulose fiber were measured by using Tensilon (Tinius Olsen) at room temperature at a crosshead speed of 20 mm/min. Brookfield viscometer (Brookfield LVDV-II+ Programmable Viscometer) and RDA (Rheometrics Dynamic Analyzer-II) were used to measure the viscosity of chemical cellulose/NMMO solution.

RESULTS AND DISCUSSION

The morphology of ascidian tunic was shown in Figure 1. The ascidian tunic has a reddish color and a texture of tangled microfibrils (see Fig. 1). This texture of the ascidian tunic is much more complex than that of wood.

The pulping process of ascidian tunic is presented in Scheme 1. From the results of the preliminary experiment of pulping, it was found that the optimum concentrations of acidic aqueous H₂SO₄ solution for prehydrolysis, alkali aqueous NaOH/Na₂S solution for digestion, and aqueous NaOCl solution for bleaching were 0.9, 9/3, and 2.9 wt %, respectively. It was also found that the effective treatment temperatures and times of prehydrolysis and cooking were about 180°C and 2 h; however, those of bleaching were about 75°C and 1 h, respectively. The bath ratio of all aqueous solutions to ascidian tunic powder was fixed at 10 : 1. Lower concentration and temperature than these conditions gave poor removal of impurities. The yield of chemical cellulose decreased markedly with an increase in the concentration of acid and alkali solutions above these concentrations, and the removal of the coloring materials of ascidian tunic was poor. The yield also decreased significantly as the treatment times of acid and alkali solutions increased.

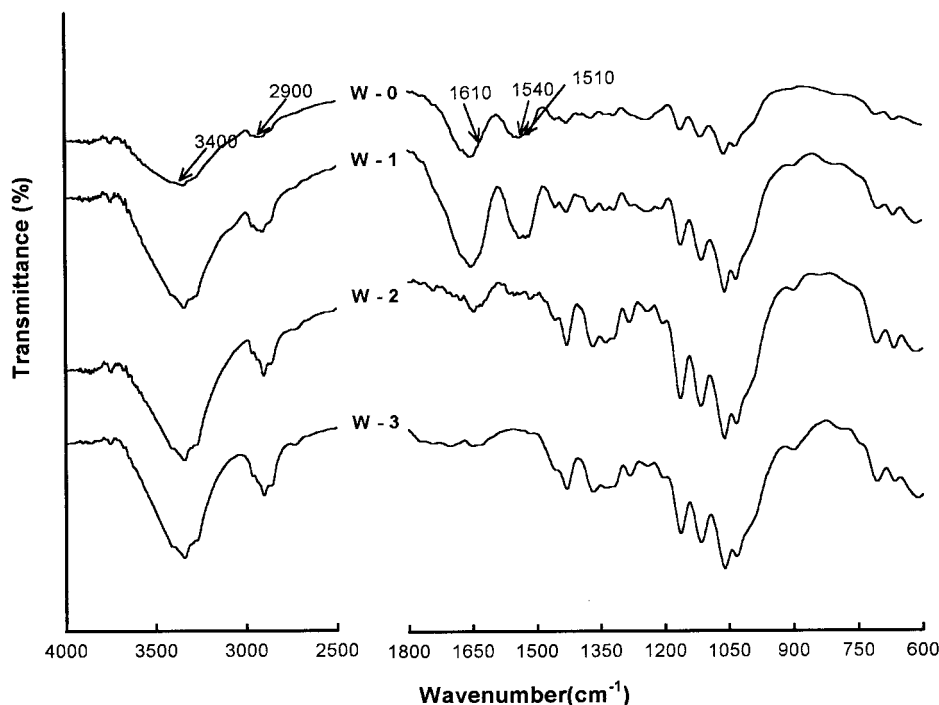


Figure 2 FTIR spectra of samples W-0, W-1, and W-2.

The sample designation and yield with treatment conditions are identified in Table I. The elements, various cellulose contents, and whiteness of samples are shown in Table II. When the ascidian tunic was treated only with acidic solution, the content of nitrogen assigned to the protein in ascidian tunic changed little. However, there was a dramatic decrease in nitrogen content up to zero ppm after treatment in alkali. The coloring materials were removed gradually by treatment steps of acid and alkali with washing; however, a little bit of reddish color still remained, and after treatment of bleaching solution, the color turned white. The JIS whiteness of the chemical cellulose prepared in this way was about 98%. The whiteness of chemical cellulose prepared in this study was almost same as that of commercial chemical cellulose. Metal components also decreased by increasing treatment steps. The yield of final sample W-3 was about 32%.

The DP_w of cellulose is determined from the Mark-Houwink-Sakurada equation by using the Ubbelohde viscometer with 1M Cuene solution as a solvent (ASTM D1795-62). The DP_w of the chemical cellulose prepared in this study was about 918. This value is a little higher than those of commercial dissolving pulps.

The α -cellulose, β -cellulose, and hemicellulose contents of samples are also shown in Table II. As the treatment step increased from sample W-0 to sample W-3, the α -cellulose content increased, but the β - and hemicellulose contents decreased. The α -cellulose content of sample W-3 was about 98%.

Infrared spectroscopy is a very useful tool for obtaining rapid information about the structure and chemical changes of organic compounds due to various treatments. This technique has used wood surface characterization for estimating the lignin and carbohydrate contents in wood and lignocellulose.⁴ The change of FTIR spectra of ascidian tunic with pulping treatment conditions was investigated in this study. The FTIR spectra of native ascidian tunic sample W-0, only acid-treated sample W-1, alkali-treated sample W-2, and final chemical cellulose sample W-3 are shown in Figure 2. All samples have a strong O—H stretching absorption band around 3400 cm^{-1} , and C—H stretching absorption band around 2900 cm^{-1} . The samples W-0 and W-1 have the aromatic skeletal vibration of lignin near 1500 and 1600 cm^{-1} . The bands at around 1510 cm^{-1} may be attributed to the C=C group of aromatic structure in lignin. The band near 1610

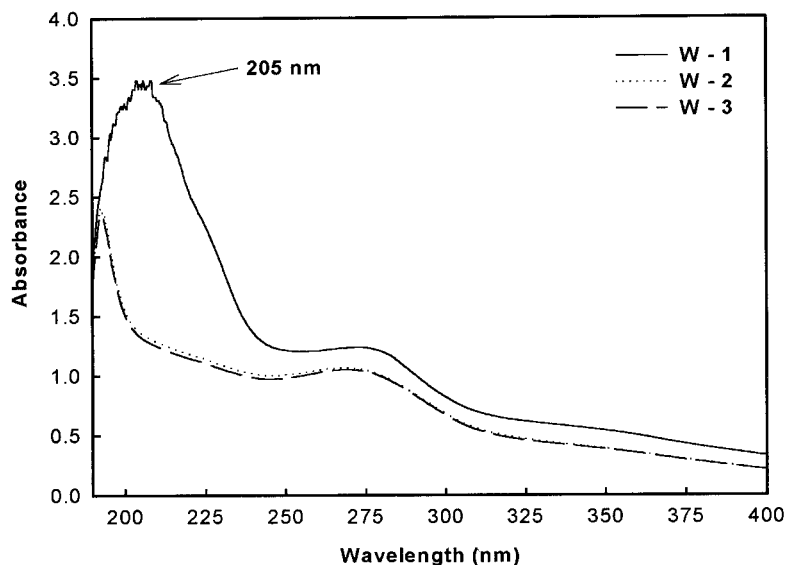


Figure 3 UV-visible absorption spectra of samples W-1, W-2, and W-3.

cm^{-1} may be due to the aromatic skeletal structure and carbonyl group of lignin. These two peaks almost did not appear in samples W-2 and W-3. This indicates that the alkali-treated sample W-2 and final chemical cellulose sample W-3 have almost no lignin component. The absorption band around 1540 cm^{-1} due to N—H stretching was observed in samples W-0 and W-1. However, this peak disappeared in samples W-2 and W-3, indicating elimination of the protein in those samples.

Generally, UV light at 205–210 and 270–280 nm wavelength is effectively absorbed by lignin.¹¹

Figure 3 shows the UV-visible absorption spectra of sample W-1, W-2, and W-3. The characteristic peaks of lignin also disappeared after treatment of alkali; however, the lignin peaks still remained in the case of acid treatment.

X-ray diffraction patterns of samples W-0, W-1, W-2, and W-3 are shown in Figure 4. Generally, native cellulose materials consisting of cellulose I crystal structure have a doublet peak at $2\theta = 14.7^\circ$ and $2\theta = 16.8^\circ$ associated with a (101) and (10 $\bar{1}$) reflections, respectively, and a singlet peak at $2\theta = 22.7^\circ$ attributed to (002) refrac-

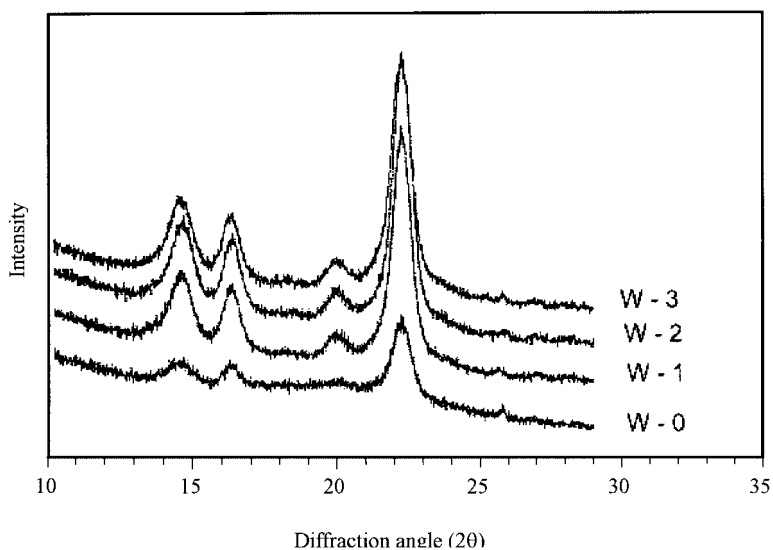


Figure 4 X-ray diffraction patterns of samples W-0, W-1, W-2, and W-3.

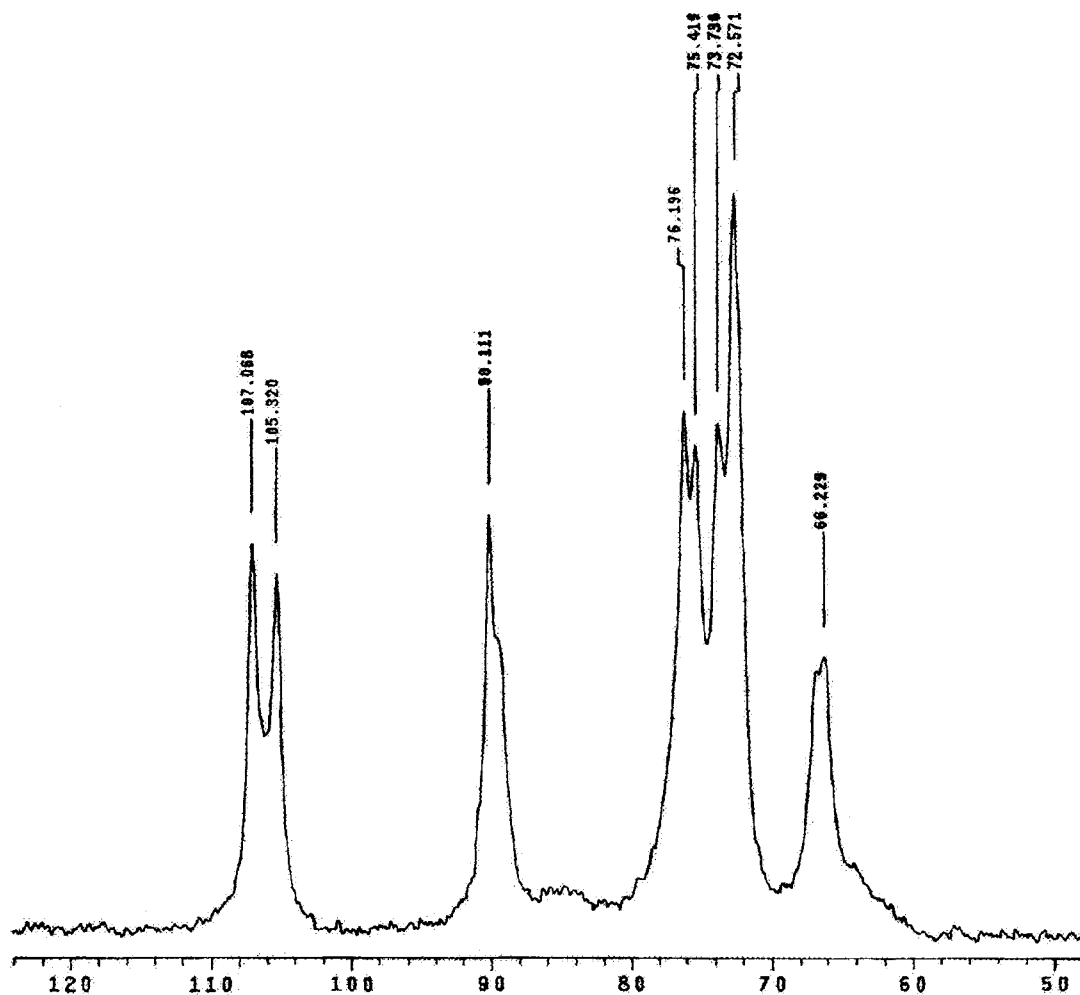


Figure 5 Solid-state ^{13}C -NMR spectrum of sample W-3.

tion.^{12,13} From the X-ray diffraction patterns, it was found that the chemical cellulose obtained here have cellulose I structure. It should be men-

tioned that various treatment conditions in this study did not alter the X-ray diffraction characteristics; however, its peak intensity changed

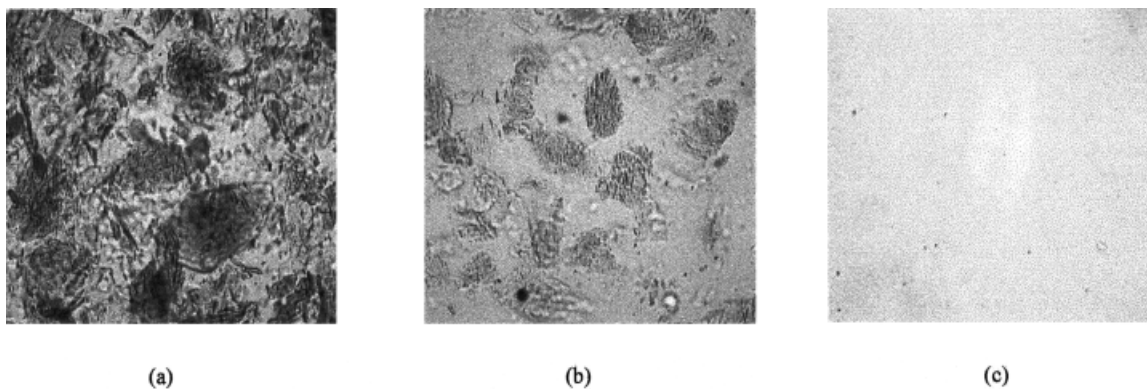


Figure 6 Photographs of chemical cellulose solutions [pulp: 6 wt %, solvent: NMMO/ H_2O (87/13 wt %)] with various dissolving times: (a) 5 min, (b) 25 min, and (c) 40 min at 120°C .

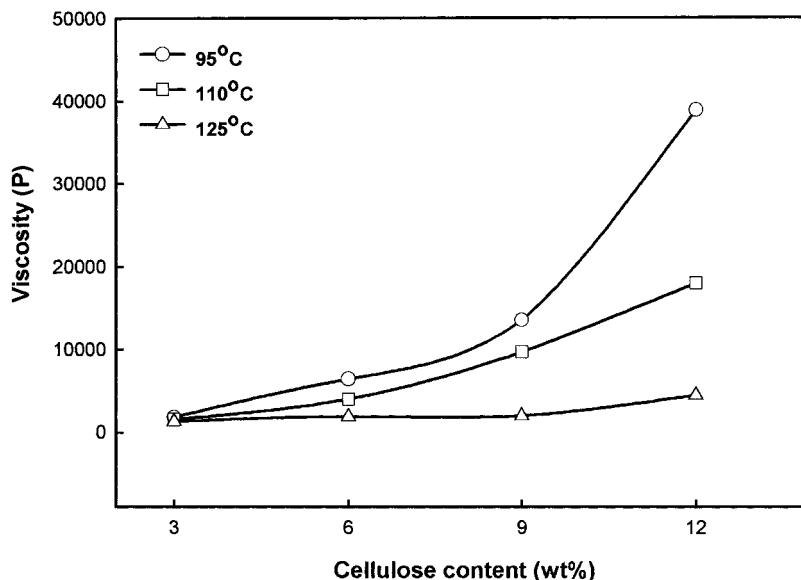


Figure 7 Relationship between viscosity and cellulose content at various temperatures.

somewhat with treatment conditions. The peak intensity increased with increasing treatment steps. This may be due to the increase of α -cellulose content by increasing treatment steps.

Atalla¹³ and VanderHart and Atalla^{14,15} revealed on the basis of solid-state ¹³C-NMR analysis of various samples that native cellulose consists of two different crystal structures, cellulose I α and I β . At the patterns of C1 resonance around

106 ppm, there appears singlet resonance for I α and doublet resonance for I β . In native cellulose samples, algal and bacterial cellulose have I α -rich structures, whereas tunicin and native celluloses of the higher plants have cellulose I β structures.¹⁶ Figure 5 shows ¹³C-NMR spectrum of sample W-3. The doublet resonance of C1 appeared near 105–107 ppm; furthermore, C4 and C6 resonance appeared near 89.1–89.9 and 65.5–

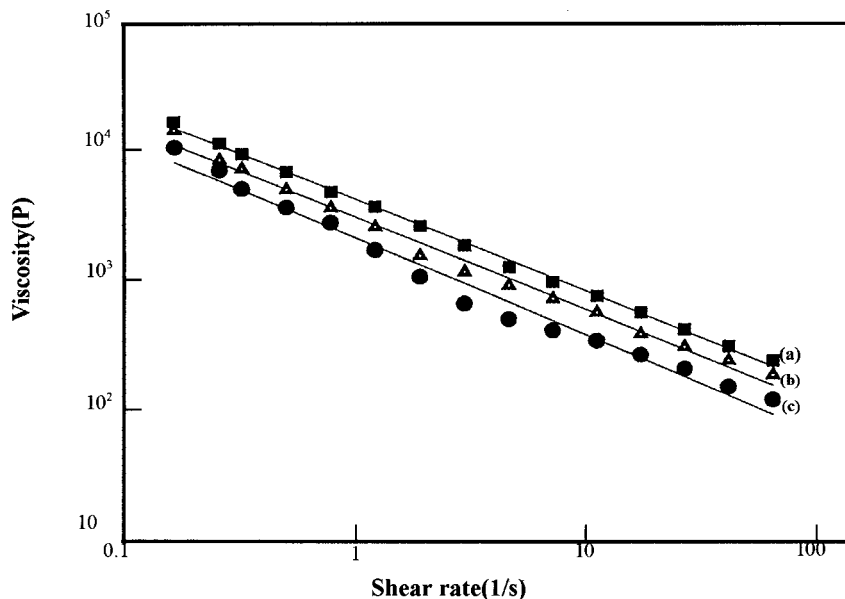


Figure 8 Relationship between viscosity of cellulose (6 wt %)/solvent [NMMO/H₂O (87/13 wt %)] and shear rate at (a) 95°C, (b) 110°C, and (c) 125°C.

66.2 ppm, respectively. From the ^{13}C -NMR spectrum, it was found that the chemical cellulose prepared in this study has cellulose I β crystal structure.

To find the optimum preparation condition of spinning dope, we observed the state of dissolution of 6 wt % pulp/solvent (NMMO/H₂O: 87/13) mixtures with dissolving time at various temperatures of 110, 120, and 130°C. Figure 6 shows the typical photograph of the dissolving state of pulp/solvent mixture with dissolving time at 120°C. It was found that it took about 45 min to reach clear solutions at 120°C. However, it took about 110 min at 110°C and about 40 min at 130°C. At a temperature of 130°C, the yellowish color of chemical cellulose/NMMO mixture turned dark in color on the surface after about 20 min, indicating the degradation of cellulose/NMMO. Therefore, the clear solution dissolved at 120°C for 45 min was used as a spinning dope in this study. The relationship between viscosity and cellulose content in cellulose/NMMO at various temperatures is shown in Figure 7. The chemical cellulose below 12 wt % could be dissolved in the NMMO/H₂O solvent at 95°C. However, as the wt % of chemical cellulose increased than this content, the chemical cellulose could no longer be dissolved clearly even at temperatures as high as 130°C. The viscosity increased with increasing cellulose content and with decreasing temperature. Figure 8 shows the viscosity of cellulose solution in various temperatures as the function of shear rate. The rheological behavior of cellulose/NMMO melt showed pseudoplastic fluid nature.

The spinning conditions and the tensile properties and crystallinity of the regenerated cellulose fibers with winding speed are shown in Table III. As the winding speed of spinning increased from 20 to 100 m/min, the tensile strength and modulus of the new regenerated cellulose fibers increased significantly; however, their elongation at break decreased slightly. The denier of fibers were in the range of 2–4; the tensile tenacity of dry and wet fibers was 3.62–4.0 and 3.55–3.95 g/d, respectively. The ratio of wet-to-dry tenacity was above 97%. This higher ratio of wet-to-dry strength may be attributed to the higher DP_w of the chemical cellulose prepared here compared to commercial chemical cellulose. Generally, the crystallinity of the fibers are determined by IR spectra¹⁷ and X-ray diffraction patterns.^{18,19} The two different crystallinities of the fibers also increased with increasing winding speed. This may be due to the elongational flow induced by winding speed.

Table III The Physical Properties of Regenerated Cellulose Fiber from W-3 with the Winding Speed (Cellulose Content: 6 wt %)

Sample Designation	Winding Speed (m/min)	Denier	Mechanical Properties								
			Initial Modulus (g/d)		Tenacity (g/d)		Elongation at Break (%)		IR Crystallinity Index	X-ray Crystallinity Index (%)	
			Dry	Wet	Dry	Wet	Dry	Wet			
C6-20	20	3.83	115.76	83.51	3.62	3.55	14.54	9.5	0.47	$(I_{002} - I_{am})/I_{002} \times 100$	76.6
C6-40	40	3.52	121.25	87.29	3.72	3.62	13.02	8.36	0.51		77.2
C6-60	60	2.92	130.15	95.27	3.97	3.88	11.09	7.25	0.63		79.4
C6-80	80	2.46	131.20	95.48	3.98	3.90	8.03	7.06	0.64		80.3
C6-100	100	2.06	137.57	103.11	4.00	3.95	6.79	6.24	0.69		80.7

CONCLUSION

Chemical cellulose was prepared from ascidian tunic by treatment of acidic aqueous H_2SO_4 solution for prehydrolysis, aqueous $NaOH/Na_2S$ solution for cooking (digestion), aqueous $NaOCl$ solution for bleaching, and acetone/water for washing. By considering α -cellulose content and whiteness of the chemical cellulose, we found that the optimum pulping conditions were as follows: The concentration of H_2SO_4 , $NaOH/Na_2S$, and $NaOCl$ were 0.9, 9/3, and 2.9 wt %, respectively, and both treatment times of acid and alkali solutions were about 2 h; the treating temperature of acid and alkali was about $180^\circ C$. The treatment temperature and time of bleaching agent were about $75^\circ C$ and 1 h. The α -cellulose content and the JIS whiteness of the chemical cellulose obtained in the optimum conditions were 98 wt % and 98%, respectively. These values are not less than those of commercial chemical cellulose. The DPw of the chemical cellulose prepared here was about 918; this value is also higher than that of the commercial one. A new regenerated cellulose fiber was prepared from the chemical cellulose by dry-wet spinning by using NMMO/water (87/13 wt %) as a solvent. The new regenerated cellulose fiber prepared in this study has a higher ratio of wet strength to dry strength (<0.97) than the general-regenerated cellulose fibers.

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