

## 미세유체시스템을 이용한 셀룰로오스 마이크로 파이버의 제조

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(2014년 11월 27일 접수, 2014년 12월 12일 수정, 2014년 12월 12일 채택)

## Microfluidic Synthesis of Microfibers Based on Regeneration of Cellulose from Ionic Liquids

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(Received November 27, 2014; Revised December 12, 2014; Accepted December 12, 2014)

**초록:** 마이크로플루이드 디바이스 내에서 셀룰로오스가 녹아있는 이온성 액체(1-에틸-3-메틸-이미다졸리움 아세테이트)로부터 셀룰로오스의 추출을 통한 직사각형의 단면적을 가지는 셀룰로오스 마이크로 파이버를 제조하였다. 본 연구에서 제안하는 방법은 빠른 시간 내에 간단하게 천연고분자 마이크로 파이버를 제작하기에 적합한 제조방법으로 적용가능하며, 이온성 액체와 주변 글리세린 용액의 유속비와 용액의 점도에 따라 다양한 크기의 셀룰로오스 마이크로 파이버를 제조하였다.

**Abstract:** Rectangular cellulose microfibers were synthesized by regenerating cellulose from an ionic liquid, 1-ethyl-3-methylimidazolium acetate, in a hydrodynamic flow-focusing microfluidic device. This technique is a fast and single-step approach for producing natural polymer microfibers. The dimensions of the cellulose microfibers were readily controlled by a simple variation of the core-sheath flow rate and the viscosity of fluids.

**Keywords:** cellulose, microfibers, microfluidic system, ionic liquids.

### Introduction

In the quest for alternatives to petroleum-based compounds, cellulose has earned distinction because of its abundance, renewability, and biodegradability.<sup>1,2</sup> Cellulose derived mainly from wood pulp has conventionally been used for producing paper, cardboard, and cellulose derivatives.<sup>2</sup> A variety of novel applications have recently emerged, where cellulose has been utilized for fibers, coatings, pharmaceuticals, composites, and hybrid materials with synthetic polymers and biomolecules.<sup>3,4</sup> However, the insolubility of cellulose in common solvents, which is due to the large proportion of strong intermolecular and intramolecular hydrogen bonds, is a critical hurdle for chemical processing of cellulose.<sup>2,5,6</sup>

The main technique used to produce the aforementioned cellulose-derived materials is viscose technology. However, this

technique requires complicated processing routes and additional facilities to treat hazardous byproducts derived from use of CS<sub>2</sub> and heavy-metal compounds in the precipitation process.<sup>2,6</sup> The Lyocell process that utilizes a direct solvent system employing *N*-methylmorpholine-*N*-oxide (NMMO) has been developed as a more environmentally benign process for producing cellulose materials.<sup>6,7</sup> Although the Lyocell process is compared to the viscose route and is almost free of effluent due to recovery of the solvent, this process still suffers from certain drawbacks, such as lack of thermal stability and high production costs.<sup>3</sup> As a prospective means of circumventing the limitations of the conventional processes, ionic liquids (ILs) have gained prominence as effective and desirable solvents for dissolving cellulose and other natural polymers. ILs offer the merits of being promising green solvents that are chemically and thermally stable with negligible vapor pressure, high dissolving capacity, and recyclability.<sup>3,8-12</sup> The proposed mechanism of cellulose dissolution in ILs involves rupture of the hydrogen bonding networks in cellulose and reformation of new hydrogen bonds between the hydroxyl pro-

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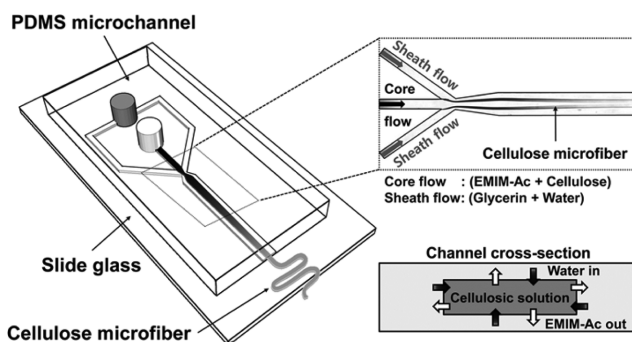
tons of cellulose and the anions of the ILs.<sup>3,11,13</sup> Cellulose materials dissolved in the ILs are regenerated by coagulation with water, and the ILs can be effectively recovered and reused.

Herein, a single-step approach for the fabrication of cellulose microfibers in a hydrodynamic flow-focusing microfluidic system is presented. This method offers the merits of simplicity, efficiency, and environmental-friendliness relative to the conventional techniques for processing cellulose into microfibers. Microchannel-based systems have been recently employed as promising tools for fabricating microfibers from synthetic polymers and hydrogels, where the advantages of continuous, reproducible production with precise control of the fiber size and morphology offered by this technique have been exploited.<sup>14-18</sup> In this study, the microfluidic synthesis of cellulose microfibers is based on the regeneration of cellulose from an IL, 1-ethyl-3-methylimidazolium acetate (EMIM-Ac), by simple contact with a glycerin-containing water phase. Unlike the typical microfibers generated via microfluidic synthesis, the device employed herein generates rectangular microfibers and the size of the cellulose fibers is controlled by changing the viscosity of the fluids and the flow rates of the cellulose solution and the surrounding sheath fluid.

## Experimental

The microfluidic device was fabricated with poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) using conventional soft-lithography. A channel master was fabricated by spin-coating SU-8 photoresist (MicroChem, Inc.) on a silicon wafer to a thickness of 50  $\mu\text{m}$  and soft-baked on a hot plate. A prepatterned photomask with the channel printout was brought into contact with the SU-8 photoresist film and exposed to UV irradiation (Model B-100A, BLAK-RAY). After post-baking, the UV-exposed wafer was developed in a SU-8 developer solution (MicroChem, Inc.) and hard-baked at 150  $^{\circ}\text{C}$  for 1 h. A mixture of the PDMS prepolymer and curing agent was then poured onto the channel master and cured at 70  $^{\circ}\text{C}$ . The polymerized PDMS replica was irreversibly bonded to a slide glass after air plasma treatment for 50 s using a plasma cleaner (Model PDC-32G, Harrick Plasma). The microchannel height was 50  $\mu\text{m}$ . The width of the microchannels for core and sheath flow injection was 90  $\mu\text{m}$  and that for cellulose fiber formation after the channel junction was 240  $\mu\text{m}$ .

A schematic diagram of the microfluidic system for the



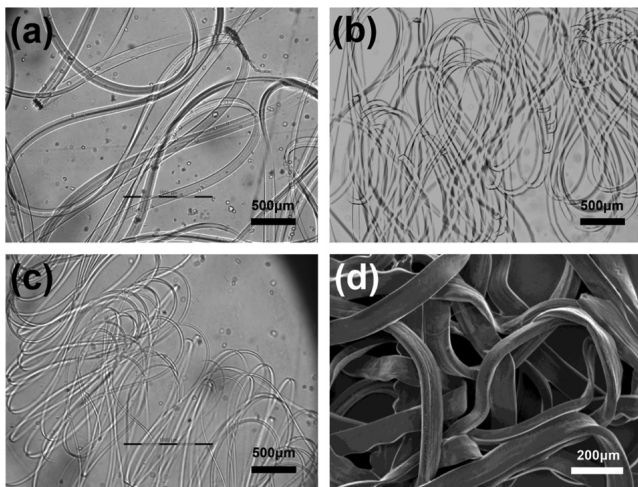
**Figure 1.** Schematic of microfluidic system for the fabrication of cellulose microfibers based on the regeneration of cellulose in the microchannel.

synthesis of cellulose microfibers is shown in Figure 1. Cellulose solutions (1 and 3 wt%) were prepared as a core flow by the dissolution of cellulose powder (Sigma Aldrich) in EMIM-Ac (Sigma Aldrich) at 100  $^{\circ}\text{C}$  for 3 h under continuous stirring. Glycerin was obtained from Sigma Aldrich. Aqueous glycerin solutions (20, 30, and 50 wt%) were used as a sheath flow. The microfluidic system for the fabrication of cellulose microfibers was placed in a Petri dish containing DI water. The core flow was injected at flow rates ( $Q_{\text{c}}$ ) of 0.1-2  $\mu\text{L min}^{-1}$  using a syringe pump (KDS-101, KD Scientific Inc.), while the aqueous sheath fluid was introduced at various flow rates ( $Q_{\text{w}}$ ) of 15-30  $\mu\text{L min}^{-1}$ .

Optical microscope images of the cellulose microfibers were obtained with an Olympus BX-51 optical microscope equipped with a high-resolution ProRes CF Scan digital CCD camera (Jenoptik). The morphology of the dried cellulose microfibers was observed with a Carl Zeiss SIGMA field emission scanning electron microscope (FE-SEM). X-ray diffraction (XRD) patterns of the cellulose powder and the cellulose microfibers were acquired with a New D8-Advance diffractometer (Bruker-AXS) using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ).

## Results and Discussion

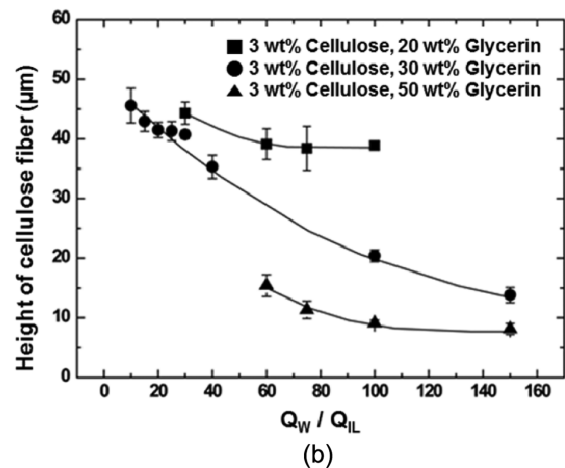
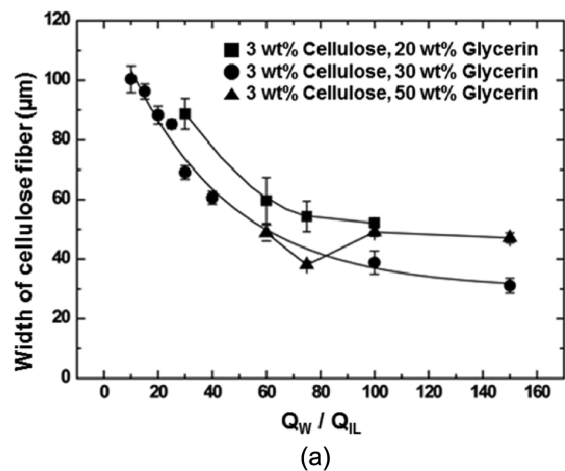
The core fluid was introduced and merged with the sheath flow in the region of the channel junction, and the jet stream of the cellulose solution dissolved in EMIM-Ac, which was surrounded by the aqueous glycerin sheath flow, described in Figure 1. The concentration gradient leads to exchange of EMIM-Ac and water at the interface between the cellulose solution and the aqueous sheath fluid. Due to the insolubility of cellulose in the aqueous phase, cellulose in the core solution



**Figure 2.** Optical microscope images of cellulose microfibrils dispersed in DI water at flow ratios ( $Q_w/Q_{IL}$ ) of (a) 15; (b) 30; (c) 100; (d) SEM image of typical cellulose microfibrils. The cellulose microfibrils were prepared with 3 wt% cellulose in EMIM-Ac and 30 wt% glycerin solution. The fibers in (d) were produced at a flow ratio of 15.

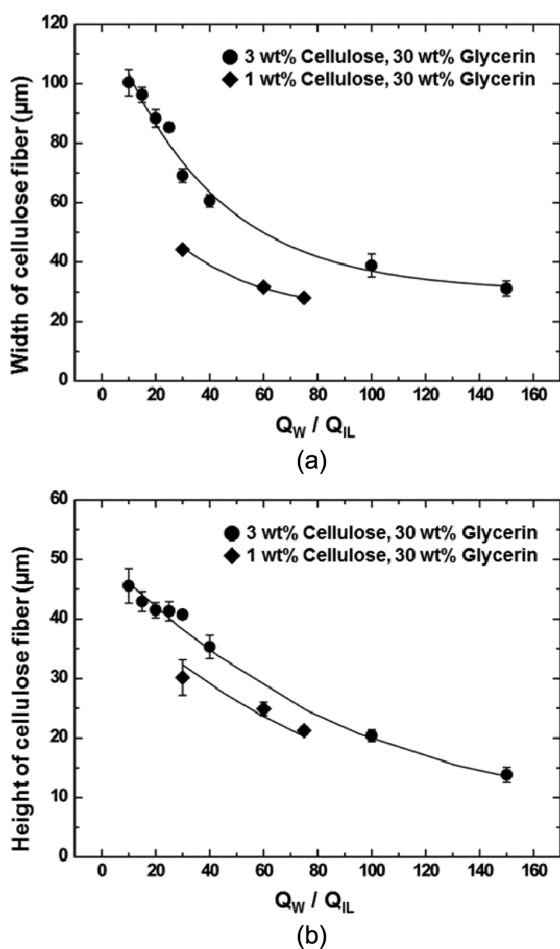
is regenerated in the form of microfibrils by coagulation with water. Thus, uniform cellulose microfibrils were continuously produced through the microfluidic device (Figure 2). The rapid coagulation of cellulose due to the high solubility of EMIM-Ac in water resulted in the formation of rectangular or belt-like microfibrils in the designed microchannel with a rectangular cross-section (Figure 2(d)).

The cross-sectional dimensions (width and height) of the cellulose microfibrils could be controlled by simply changing the flow ratio ( $Q_w/Q_{IL}$ ) of the aqueous sheath and cellulose core fluids. As the flow ratio increased, cellulose microfibrils with smaller dimension of the rectangular cross-sections were produced (Figure 1(a)-(c)) because the higher flow ratio between the sheath and core fluids induces greater shearing and stretching of the cellulose solution due to the increased shear stress in the microchannel.<sup>15,19</sup> The shear stress ( $\tau$ ) at the solid surface between parallel plates under parabolic flow can be approximated based on the flow properties and channel geometry:<sup>20,21</sup>  $\tau = 6 \mu Q/h^2 w$ , where  $\mu$  is the fluid viscosity,  $Q$  is the flow rate, and  $h$  and  $w$  are the height and width of the channel, respectively. Although this estimate may differ from the actual shear stress at the surface of the cellulose microfibrils in the channel, it represents a reasonable and qualitative approximation of the effect of shearing on the fiber size due to variation of the fluid viscosity and flow ratio in the present device. To evaluate the effects of shearing on the fiber dimensions, cellulose microfibrils were prepared with 3 wt%



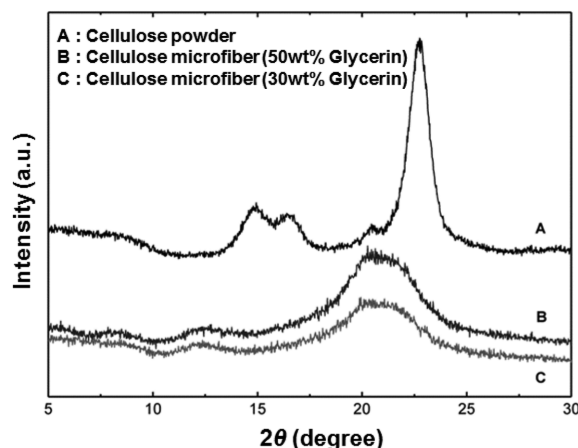
**Figure 3.** (a) Width; (b) height of cellulose microfibrils as a function of flow ratio ( $Q_w/Q_{IL}$ ) using different concentrations of glycerin solution.

cellulose in EMIM-Ac using different concentrations of glycerin solution (20, 30, 50 wt%) and various flow ratios. After washing the obtained microfibrils with DI water to remove the remaining EMIM-Ac, the width and height of the cellulose microfibrils dispersed in DI water were measured (Figure 3). As our anticipation, the width and height of the cellulose microfibrils decreased in response to the increase in the flow ratio of the sheath and core solutions. Although an initial increase of the fiber width was observed with the use of 50 wt% glycerin solutions at flow ratios higher than 80 due to the unstable flow through the microchannel, the dimensions of the cellulose microfibrils decreased with the use of higher glycerin concentrations due to the increase in the viscosity of the aqueous sheath fluid. This reduction of the fiber size is derived from the greater shear stress experienced by the cellulose microfibrils that solidified in the microchannel at higher flow ratios and with more viscous sheath flow.



**Figure 4.** (a) Width; (b) height of cellulose microfibers as a function of flow ratio ( $Q_w/Q_{IL}$ ) using different concentrations of cellulose solution.

The size of the cellulose microfibers could also be controlled by changing the concentration of cellulose in the IL. Figure 4 presents a comparison of the fiber dimensions obtained with two different concentrations of cellulose (1 and 3 wt%) using a glycerin concentration in the sheath flow of 30 wt%. With increasing the flow ratio, the width and height of the cellulose microfibers produced using 1 wt% cellulose reduced due to the high shearing effect, and the reduction was larger than observed for the cellulose fibers produced using 3 wt% cellulose. In addition, cellulose fibers produced from 1 wt% cellulose were broken in the microchannel at higher flow ratios ( $Q_w/Q_{IL} > 80$ ). The cellulose fibers formed in the microchannel using the lower concentration of cellulose have a softer and thinner solidified surface, leading to greater stretching or breaking of the fibers at the same flow ratio and glycerin concentration used for producing the fibers with the higher cel-



**Figure 5.** XRD patterns of pristine cellulose powder and cellulose microfibers. Cellulose microfibers were prepared with 3 wt% cellulose in EMIM-Ac at a flow ratio of 30.

lulose concentration.

XRD patterns of cellulose powder and cellulose microfibers are presented in Figure 5. Typical diffraction peaks of cellulose I were observed at  $2\theta = 14.8$ ,  $16.3$ , and  $22.6^\circ$  in the XRD pattern of pristine cellulose, whereas the XRD pattern of the cellulose microfibers (after the regeneration of cellulose in the microchannel) was consistent with the cellulose II structure; this transformation of the cellulose structure is similar to that of typical ILs.<sup>22,23</sup> The reduced intensity of the diffraction peaks of the cellulose microfibers compared to those of the cellulose powder indicates that the crystallinity of the regenerated cellulose is lower than that of pristine cellulose. Rapid regeneration of cellulose in the microchannel may impede restructuring the original crystalline form of cellulose after breaking the hydrogen bonds during the dissolution of cellulose in EMIM-Ac.

## Conclusions

In summary, a simple and reproducible approach for producing cellulose microfibers by applying microfluidic technology was developed. The size of the cellulose fibers was easily controlled by varying the flow ratio and fluid viscosity. No similar methods have been reported for the microfluidic synthesis of cellulose microfibers based on the regeneration of cellulose using ILs. The precise control of material fabrication in microfluidic systems enables the realization of complex microstructures (tubes, capsules, rods, etc.,) for various applications using regenerated cellulose, as we intend to disclose in a further publication.

**Acknowledgements:** This study was supported by a grant from the Korean Health Technology R&D Project, Ministry of Health & Welfare (Grant No. HN10C0032) and the Chung-Ang University Excellent Student Scholarship in 2013.

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