

## Dissolution and modification of cellulose using high-pressure carbon dioxide switchable solution



Phawinee Nanta<sup>a,b</sup>, Wanwisa Skolpap<sup>a</sup>, Kittiwut Kasemwong<sup>c</sup>, Yusuke Shimoyama<sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Pathumthani, 12120, Thailand

<sup>b</sup> Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 S1-33, Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

<sup>c</sup> NANOTEC Research Unit, National Nanotechnology Center, National Science and Technology Development Agency, 130 Thailand Science Park, Paholyothin Rd., Khlong Luang, Pathumthani, 12120, Thailand

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### ABSTRACT

High-pressure carbon dioxide switchable solution with 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and ethylene glycol (EG) was applied for a dissolution and modification of cellulose derived from a cassava pulp waste. The switchable solution of DBU and EG were formed by adding carbon dioxide under a pressure range of 0.1–10.0 MPa and a temperature range of 298 and 333 K. The cellulose was dissolved into the CO<sub>2</sub> switchable system at a pressure of 0.1 and 5.8 MPa and a temperature of 313 K. The precipitates of bicarbonate salt of reaction between DBU and carbon dioxide were observed in the switchable solution at the higher pressures and lower temperatures. The cellulose was also modified in the switchable solution with the ionized DBU, EG and carbon dioxide as analyzed by Fourier transform infrared spectroscopy. The modified cellulose was then utilized for the fabrication of the transparent film.

### 1. Introduction

Dissolution of cellulose has aimed to prepare a regenerated cellulose or to modify cellulose chemically in a homogeneous environment. Some challenges in the cellulose dissolution using common solvents are strong intra- and inter- molecular hydrogen bonding and a stable crystalline structure of the cellulose. A variety of cellulose dissolution techniques are designed to achieve homogeneous solution dissolving cellulose on the modification to desirable chemical properties and functionalities [1]. The effective cellulose dissolution technologies such as aqueous system containing metal have been developed [2,3]; however, these solutions do not promise for the cellulose dissolution due to their toxic byproducts released into the environment. Although ionic liquids (ILs), a potential solvent with high levels of product recovery and solvent recyclability [4], has been suggested as high effective solvent for the homogeneous solution of cellulose [5]. The halide anions in ILs are relatively high viscosity resulting in processing difficulty during the dissolution process. Moreover, the applications of ILs pertain to the serious drawbacks that ILs might chemically react with the cellulose or physically entrap the cellulose on the modification and regeneration processes. The reaction or entrapment of cellulose could give the undesirable effects on physical, chemical and biological properties of the final cellulose product [6].

Carbon dioxide, nontoxic, nonflammable and environmentally acceptable gas has been gained more attractive on the development of the chemical or biochemical processes at high-pressure conditions in the recent years [7–10]. The high-pressure carbon dioxide has unique properties, both the diffusivity like a gas and high solubility like a liquid. In meanwhile, Jessop et al. have reported a switchable polarity of the solvent by carbon dioxide [11]. This switchable effect by carbon dioxide has been extended to the triggered or switchable properties of the solvent polarities, surfactant, polymer, gel, and catalyst [12]. A switchable polarity ionic liquid by carbon dioxide was reported by Liu et al. [13]. Yilmaz and Soylak [14] have studied a liquid phase microextraction in the switchable polarity solution by carbon dioxide. The switchable technique by carbon dioxide has been also applied for the emulsification techniques [15,16]. Li et al. studied the preparation of carbon dioxide switchable emulsion with hydrophobic amines for the oil and water separation [15].

Carbon dioxide switchable system has been applied to cellulose techniques, such as a cellulose nanocrystal (CNC) modification with 1-(3-aminopropyl)imidazole (APIm) and controlling of dispersion properties [17]. The prepared CNC-APIm formed a stable dispersion and aggregation in water with and without carbon dioxide. Dissolution of cellulose with carbon dioxide in the switchable system has also been studied by Yang et al. [18]. A rapid and effective derivative dissolution

\* Corresponding author.

E-mail address: [yshimo@chemeng.titech.ac.jp](mailto:yshimo@chemeng.titech.ac.jp) (Y. Shimoyama).

of cellulose pulp was achieved in the presence of carbon dioxide and 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU). The solution containing 1,1,3,3-tetramethyl guanidine (TMG) and ethylene glycol in the presence of carbon dioxide were applied as a solvent of the cellulose [19]. It is expected that the combination of the switchable solution with high-pressure carbon dioxide could achieve the effective dissolution and chemical modification of the cellulose because of the high solubility of the high-pressure carbon dioxide into the solution [20].

In this work, the switchable solution using high-pressure carbon dioxide is employed in the dissolution and modification of the cellulose. The switchable solution in the presence of carbon dioxide is prepared using ethylene glycol and 1,8-Diazabicyclo [5.4.0] undec-7-ene which is a carbon dioxide capturing agent and strong base, correspondingly. The phase behavior during the dissolution of the cellulose in the switchable solution at high pressures was studied at various temperature and pressure. The molecular vibration and thermal properties of the cellulose modified in the high-pressure switchable solution are also discussed. The modified cellulose in the switchable solution was also used for the fabrication of its thin film.

## 2. Experimental section

### 2.1. Materials

Cellulose used in this work was prepared by an extraction cassava pulp waste (CHOLCHAROEN GROUP, Thailand). Thirty grams of cassava pulp waste were removed hemicelluloses and lignin by alkaline treatment with 750 ml of 4% sodium hydroxide at 393 K for 1 h. The resulting brown precipitates were filtered and washed with tap water until reaching to the neutral condition. To remove lignin, the neutral precipitates were mixed with 375 ml of 1% sodium chlorite and were then adjusted pH to 5 with 4% acetic acid. The mixture was transferred to a capped bottle and stirred in water bath at 353 K for 24 h. After being cooled, the white precipitates were filtered and washed with tap water until being the neutral. For preparation of the cellulose powder, 750 ml of distilled water was added to the neutral white precipitates, mixed with homogenizer at 8000 rpm for 5 min, and spray-dried at inlet temperature of 403 K, 0.5 MPa and 20 ml min<sup>-1</sup> of the spraying rate.

1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU), ethylene glycol (EG), dimethyl sulfoxide (DMSO) were purchased from Wako Pure Chemical Industries, Ltd. Carbon dioxide (99.95%) was supplied from Fujii Bussan Co. Ltd.

### 2.2. Experiments

#### 2.2.1. Phase behavior during dissolution and modification of cellulose

Cellulose powder was installed into the solution of DBU and EG with a molar ratio of 2:1. The concentration of cellulose in the solution was 4 mg ml<sup>-1</sup>. The cellulose suspension was mixed with DMSO in the twice volume of the suspension. The suspension was used for the dissolution and modification of the cellulose by high-pressure carbon dioxide using the setup as shown in Fig. 1. The set up is very similar to that used for the titanium sol-gel reaction in supercritical carbon dioxide as given in the literature [21]. The cellulose suspension, 1.50 ml was put in a high-pressure vessel with view window in advance. Carbon dioxide from the gas cylinder was cooled by the chiller and got to liquid state. A check valve (Swagelok) was equipped for preventing from a reverse flow. The liquefied carbon dioxide was pressurized by double plunger pump (NP-D-321 from Nihon Seimitsu Co. Ltd., Saitama, Japan). The pressure of the system was controlled by a back pressure regulator (26-1700 Series from TECOM™). The pressurized carbon dioxide was heated by flowing through a preheating coil and installed into the high-pressure vessel heated by several cartridge heaters. The phase behavior during the dissolution and modification of the cellulose was observed through the view window with microscope digital camera

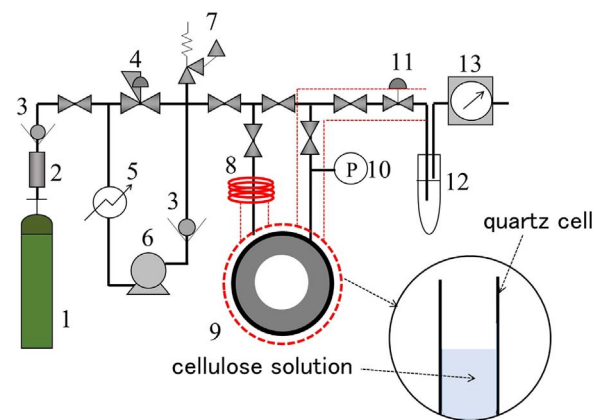


Fig. 1. Schematic diagram of setup for phase behavior of switchable solution during cellulose dissolution. 1; CO<sub>2</sub> cylinder, 2; silica gel cell, 3; check valve, 4; back pressure regulator, 5; chiller, 6; double plunger pump, 7; safety valve, 8; pre-heating coil, 9; high-pressure vessel, 10; pressure gauge, 11; needle valve, 12; solvent trap, 13; wet type gas flow meter.

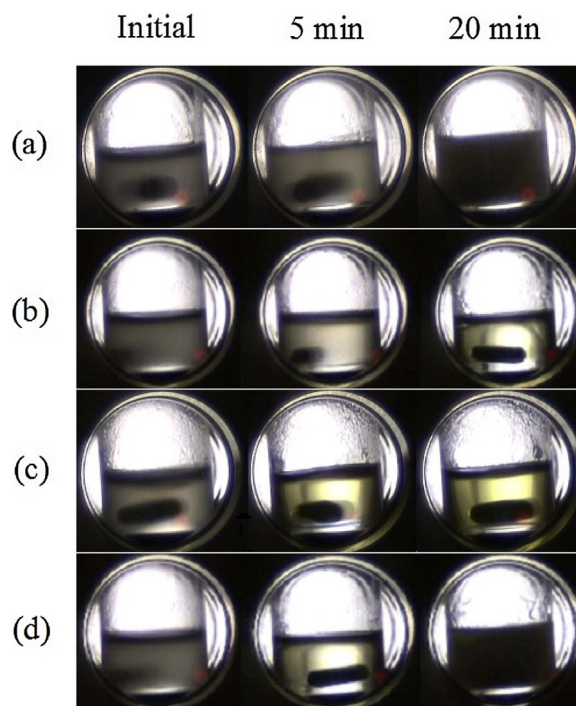


Fig. 2. Phase behavior during dissolving cellulose in high-pressure CO<sub>2</sub> switchable solution. (a) 298 K and 5.6 MPa, (b) 313 K and 5.8 MPa, (c) 333 K and 5.8 MPa, (d) 333 K and 10.0 MPa.

with 32 modifications (SPACE Inc.). The dissolution and modification of the cellulose were conducted for 2 h at 0.1–10.0 MPa and 298–333 K. The inlet pressure of the high-pressure vessel was controlled by the back pressure regulator. The system was depressurized through a needle valve (6136G4Y, HOKE) up to atmospheric pressure after the dissolution and modification operations. The modified cellulose in the high-pressure switchable solution was removed from the high-pressure vessel after the depressurization and then used for the fabrication of its film as described in Section 2.2.3.

#### 2.2.2. Phase boundary on dissolution of cellulose in switchable solution

The cellulose suspension was also used for the determination of the phase boundary on the dissolution of the cellulose in a high-pressure carbon dioxide switchable system using the setup in Fig. 1. The cellulose suspension was installed into the high-pressure vessel before

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