



Title	Direct Electrospinning of Cellulose Acetate onto Polyurethane Sheet and Effect of Its Saponification on Mechanical Properties
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1                   **Direct Electrospinning of Cellulose Acetate onto**  
2                   **Polyurethane Sheet and Effect of Its Saponification on**  
3                   **Mechanical Properties**  
4

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12   **Abstract**

13   This paper demonstrates direct electrospinning of two kinds of cellulose acetate, water-soluble  
14   cellulose acetate (WSCA) and cellulose diacetate (CDA), onto a non-conductive synthetic polymer  
15   sheet to modify its surface morphology. Polyurethane (PU) sheets for polishing compact and hard  
16   disks were used as an example of synthetic polymer sheet. The direct electrospinning of WSCA 11  
17   wt.% in aqueous ethanol solution (40 wt.%) and CDA 9 wt.% in aqueous acetone solution (90  
18   wt.%), were carried out by spraying anti-static agent onto the sheet. However, the electrospun  
19   fibers were easily peeled off from the PU sheet. Tight fixation of the fibers was achieved by  
20   spraying a 50 wt.% of dimethylformamide/ethanol solution additionally during the spinning.  
21   Finally, the cellulose acetate fibers on the PU sheet were converted to regenerated cellulose fibers  
22   by leaving the fibers in an ammonia atmosphere for complete saponification. Change in surface  
23   morphology was evaluated by tribology test in addition to microscopic observations. Friction  
24   coefficient of PU sheet was dramatically decreased with increasing the amount of WSCA and  
25   CDA fibers deposited, suggesting that the PU sheet surface became smoother. Most of friction  
26   coefficients of the sheet were slightly increased by saponification, except for that of the PU sheet  
27   with increased amount of WSCA fibers, which might be attributed to the change in the elasticity  
28   upon saponification.

29  
30   **Keywords:** Electrospinning · Cellulose acetate · Surface modification · Saponification·  
31   Regenerated cellulose · Tribology test

32

33

**35 Introduction**

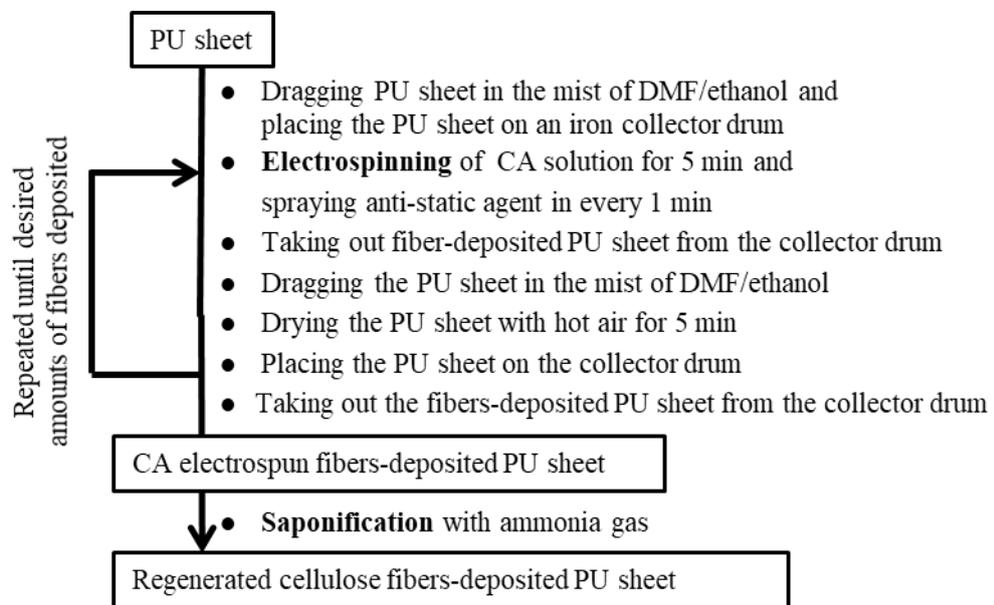
36 Cellulosic materials, cellulose nanofiber (CNF) (Yano *et al.*, 2005; Ito, 2013; Kakroodi *et al.*, 2014; Wang *et al.*, 2014), and other cellulose derivatives (Sugimura *et al.*, 2013; Lee *et al.*, 2014; Sugimura *et al.* 2015; Li *et al.*, 2018) have drawn much attention as a filler for plastics (Sakakibara *et al.*, 2017), because they have much higher specific elastic modulus than steel (Nogi *et al.*, 2009; Orts *et al.*, 2005). In general, CNF has cellulose I crystalline polymorph. The elastic modulus of the crystalline region in cellulose I is reported to be around 135 GPa (Sakurada *et al.*1962; Nishino *et al.*1995; Matsuo *et al.*1990). Regenerated cellulose shows cellulose II polymorph (Wang *et al.* 2014; Sarko & Muggli 1973) whose elastic modulus is also reported to be about 110 GPa by X-ray diffraction analysis (Matsuo *et al.*1990) and about 160 GPa by theoretical estimation (Tashiro & Kobayashi 1991). Such elastic moduli are also much higher than those of plastics (Sakurada *et al.*1964). Therefore, cellulosic materials are used as a filler (Sakakibara *et al.* 2017; Chupin *et al.* 2017) to improve the mechanical property of plastics (Yano *et al.*, 2005; Borja *et al.*, 2005). It is considered that the cellulosic materials can be utilized as a surface modification agent to alter the surface property of plastics, such as morphology and mechanical property.

51 There are two possible methods proposed; solution coating and direct deposition of solid material for the surface modification of plastics with cellulose derivatives. The solution coating method may not bring high mechanical strength to the surface of plastics, because the regenerated material like film from the solutions normally amorphous and shows low elastic modulus. By contrast, direct deposition method using solid materials, such as fiber, would probably give the high elasticity to surface, because the deposited material, for example CNF, keeps high crystallinity and elastic modulus in this method. However, it is anticipated to be very difficult to spray CNF coating onto plastics, because CNF is generally produced as a viscous aqueous suspension like hydrogel (Abe and Yano, 2012) and a spraying machine for viscous hydrogel is not popular or rarely available. In addition, water evaporation after coating the CNF gel could also be a bottleneck, because it takes a long time. Hence, electrospinning seems to be a promising, alternative method for deposition of cellulosic materials. The electrospun mat has a higher Young's modulus than the cast film does (Subramanian *et al.*, 2008). Thereby, if the direct electrospinning of cellulose onto plastics is possible, this method must bring the high elasticity to plastic surface.

65 A concept of electrospinning was proposed in the 16<sup>th</sup> century, and melt- (Norton and Mass, 1936) and dry-electrospinning (Formhals, 1934) was patented in 1930's. Thus, electrospinning is a very old technique. Besides such types of electrospinnings, wet-electrospinning is also available. In the dry-electrospinning with polymer solution, charged polymer solution flies as a jet from a nozzle to a collector by electric force together with the evaporation of solvent used (Hou *et al.*, 2012; Bhardwaj & Kundu, 2010). During the flying, polymer molecules are elongated and orientated by the electric force. It is, therefore, expected that the regenerated electrospun fibers are crystallized (Zheng *et al.*, 2007; Kongklang *et al.*, 2008; Nicosia *et al.*, 2016). Cellulose derivatives, for example, cellulose acetate (CA), which dissolves in

74 volatile organic solvents, can be electrospun by this method. In 1934, electrospinning of CA was  
 75 first reported (Formhais, 1934). Other researchers successfully prepared fine regenerated cellulose  
 76 fibers by electrospinning of CA followed by saponification (Ok *et al.* 2008, Zhang *et al.* 2008,  
 77 Huang *et al.* 2011, Stephen *et al.* 2011, Rodri'guez *et al.* 2012). Although cellulose cannot be  
 78 directly spun by the dry-electrospinning, electrospun fibers of cellulose can be obtained by wet-  
 79 electrospinning. In the wet-electrospinning, polymer molecule in the solution is also elongated by  
 80 the electric force and is regenerated in a coagulation bath with a non-solvent. Frey *et. al* (2008)  
 81 summarized the wet-electrospinning of cellulose, where water was used as a coagulant for  
 82 cellulose solutions in aqueous N-methyl-morpholine N-oxide solution and in lithium  
 83 chloride/dimethylacetamide, and ethanol as a coagulant for cellulose solutions in 1-butyl-3-  
 84 methylimidazolium chloride and 1-ethyl-3-methylimidazolium benzoate. However, there is no  
 85 report on melt-electrospinning of cellulose, as far as we know.

86 We consider the dry-electrospinning of CA is a promising technique for direct deposition  
 87 of cellulose onto plastics. Kakunuri *et al.* (2017) reported that CA nanofiber was directly  
 88 electrospun on nylon mesh sheet, which was placed on an iron collector, for producing air filter.  
 89 We also confirmed that direct electrospinning on the mesh sheet was successful. However, there is  
 90 no report on direct dry-electrospinning on non-mesh polymer sheet or film. The reason is probably  
 91 attributed to non-electroconductivity of plastics. Static charge is accumulated on the plastics  
 92 during the electrospinning. As a result, the voltage difference between a nozzle and plastics on the  
 93 iron collector disappears, and the solution jet flies to other parts in the electrospinning system, but  
 94 never arrives at the plastics on the collector. Therefore, an aim of this study is to develop a direct  
 95 dry-electrospinning method of cellulose onto plastics together with a fixation method.



96 **Fig. 1.** Preparation strategy of regenerated cellulose fibers-deposited PU sheet.

97 To achieve the objective, we made a preparation strategy (**Fig 1**), which was composed of  
 98 three parts: electrospinning, fixation, and saponification. In this study, polyurethane (PU) sheet  
 99 with rough surface was used as a non-mesh polymer sheet. The PU sheet was developed as a  
 100 polishing pad (Ho *et al.*, 2016; Budinger, 1990) for hard disks and compact disks. Another reason

101 why the PU sheet was chosen is the ease to detect morphological change upon the electrospinning  
102 and to evaluate surface mechanical properties. Two kinds of CAs, water-soluble cellulose acetate  
103 (WSCA) and cellulose diacetate (CDA) were used as cellulose. WSCA, which was produced as a  
104 research sample by Daicel Company (Osaka, Japan), can be dissolved in environmentally-benign  
105 solvents, such as water and aqueous ethanol. On the other hand, CDA could be dissolved in other  
106 types of solvent, such as acetone and *N,N*-dimethylformamide (DMF). Accordingly, first process  
107 is direct electrospinning of both CAs onto the PU sheet, and second process is to tightly fix  
108 electrospun fibers on the sheet. As the final process, the CA electrospun fibers are converted into  
109 regenerated cellulose by saponification to obtain fine regenerated cellulose fibers-deposited PU  
110 sheet. Change in mechanical properties of PU sheet surface by these processes is monitored by  
111 tribology test.

112

## 113 **Experiment**

### 114 **Materials**

115 Water-soluble cellulose acetate (WSCA) with a degree of substitution (DS) of 0.9 and  
116 cellulose di-acetate (CDA) with a DS of 2.4 were kindly supplied from Daicel Corporation, Ltd.,  
117 (Osaka, Japan). DMF, acetone, ethanol, acetic acid and aqueous NH<sub>3</sub> (28%) were purchased from  
118 Wako Pure Chemical Ltd., (Tokyo, Japan). An anti-static agent (staticide: 99.8% of anhydrous  
119 isopropyl alcohol) was purchased from ACL Inc. (Chicago, IL, U.S.A.). Fifty to 90 wt.%  
120 DMF/ethanol solutions were prepared. As a polishing agent for compact disc (CD) and hard disc  
121 (HD), polyurethane (PU) sheet with poly(ethylene terephthalate) (PET) as a supporting film was  
122 provided from Fujibo Ehime Co., Ltd. (Saijo, Japan) (**Supplementary Figure S1**). Stainless steel  
123 plate for tribology measurement was purchased from Yamamoto-MS Co., Ltd. (Tokyo, Japan).

### 124 **Electrospinning**

#### 125 *Simple electrospinning of WSCA and CDA on aluminum foil and PU sheet*

126 WSCA was dissolved at 50 °C in 40 wt.% aqueous ethanol solution to give its solutions at  
127 concentrations of 1-17 wt.%. CDA was dissolved in 90 wt.% aqueous acetone solution to give its  
128 solutions at concentrations of 1-17 wt.%.

129 The cellulose acetate (CA) solutions were inserted into a glass syringe with a stainless-  
130 steel needle (inner diameter, 0.70 mm), and then the syringe was set in an electrospinning  
131 apparatus manufactured at Machinery Laboratory, Graduate School of Science, Hokkaido  
132 University. Aluminum foil and PU sheet was separately rolled on an iron drum as a collector, after  
133 electrodes were connected to the syringe nozzle and the iron collector. When using PU sheet, the  
134 anti-static agent was sprayed onto the sheet for a few second in every 1 min during electrospinning.  
135 The syringe was pressed with a syringe pump (YMC Co., Ltd., Kyoto, Japan) at a flow rate of 1.0  
136 mL/h. The electrospinning conditions were as follows: distance between the nozzle and the  
137 collector, 10 cm; applied voltage, 18 kV; rotational rate of the collector, 115 rpm; spinning  
138 temperature, 30°C; relative humidity, 22%. To control the humidity and the temperature, a  
139 dehumidifier and a room heater were used during spinning.

140

#### 141 *Preparation of electrospun CA fibers fixed on PU sheet*

142 Before spinning, a 50 wt.% DMF/ethanol solution was sprayed in the air by using a  
143 typical sprayer, which was normally used for watering plant. An intact PU sheet (115.14 cm<sup>2</sup>) was  
144 dragged for 3 s in the solvents mist. The dragging process was repeated 3 times. The resultant PU  
145 sheet was rolled on the iron collector. Electrospinning of both CAs together with spraying the anti-  
146 static agent was carried out according to the above conditions. After 5-min electrospinning, the  
147 fiber-deposited PU sheet was taken out of the collector, and the sheet was dragged in the mist of  
148 mixed solvent followed by drying with a hair dryer for 5 min. The dried PU sheet was set again on  
149 the collector, and electrospinning was conducted again. This process was repeated until desired  
150 amount of CA fiber were deposited on the PU sheet. Finally, the fiber-deposited PU sheet was  
151 dried overnight *in vacuo* at 60 °C.

#### 152 **Saponification of CA fibers**

153 The CA fiber-deposited PU sheet was cut into pieces (about 6 × 3.79 cm<sup>2</sup>), and the  
154 resultant PU sheets were placed in a petri-dish (9 cm in diameter). About 50 mL of 28% NH<sub>3</sub>  
155 aqueous solution was poured into another petri-dish (9 cm in diameter). Both petri-dishes were  
156 placed in a large petri-dish (20 cm in diameter). Top of the large dish was covered with another  
157 large dish, and this set of petri-dishes was sealed with para-film and cooking wrap. The dish-set  
158 was left standing for one week at room temperature. The PU sheets were then taken out of the  
159 petri-dish and washed with distilled water. The PU sheets were dried *in vacuo* overnight at room  
160 temperature.

#### 161 **Tribology test**

162 The CA fiber-deposited PU sheet with the fiber amounts of 0.81, 1.61 and 3.20 g/m<sup>2</sup> was  
163 cut into pieces (about 6×3.8 cm<sup>2</sup>), and the resultant PU sheet was attached as a specimen with  
164 double-sided tape on an aluminum plate and then placed on a tribogear instrument (HHS3000:  
165 Shinto Science Co., Ltd, Tokyo, Japan). During the measurement, an aluminum ball as a load  
166 probe was allowed to move on the specimen under different loads. The tribology test conditions  
167 were as follows: working distance, 30 mm; scan rate, 2 mm/sec; reciprocation times, 10; loads, 5 -  
168 150 gf. The friction coefficients were calculated from the friction forces measured and the load of  
169 probe.

#### 170 **Instrumental analysis**

171 The crystallinity of the CA fiber was determined using an X-ray diffractometer (Rigaku,  
172 Tokyo, Japan). Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the  
173 samples were recorded with an FT/IR-4100 spectrophotometer (Jasco Co., Tokyo, Japan). The  
174 morphology of the electrospun CA fibers was observed under a 3-D microscope (violet laser color  
175 3-D profile microscope, VK-9510: Keyence, Osaka, Japan).

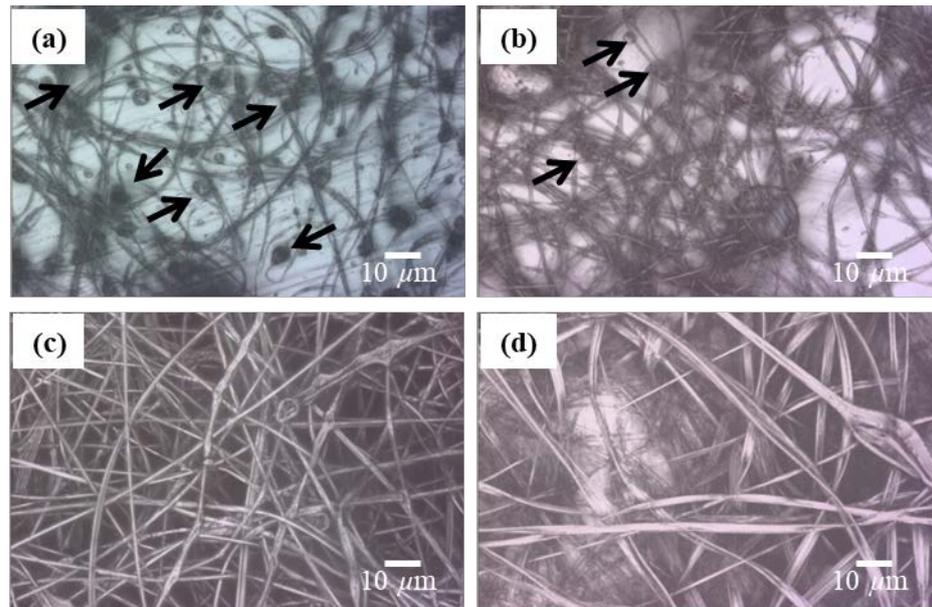
176

#### 177 **Results and discussion**

##### 178 **Electrospinning of WSCA and CDA**

179 In this study, WSCA and CDA were used as a CA sample to prepare electrospun fibers.  
180 WSCA can be dissolved in aqueous ethanol at concentrations of 0-70 wt.%. In the case of CDA, it  
181 was dissolved in aqueous acetone at concentrations of 60-100 wt.%. Several spinning dopes at  
182 different CA concentrations (7, 9, 11 and 15 wt.%) and at different concentrations of the aqueous

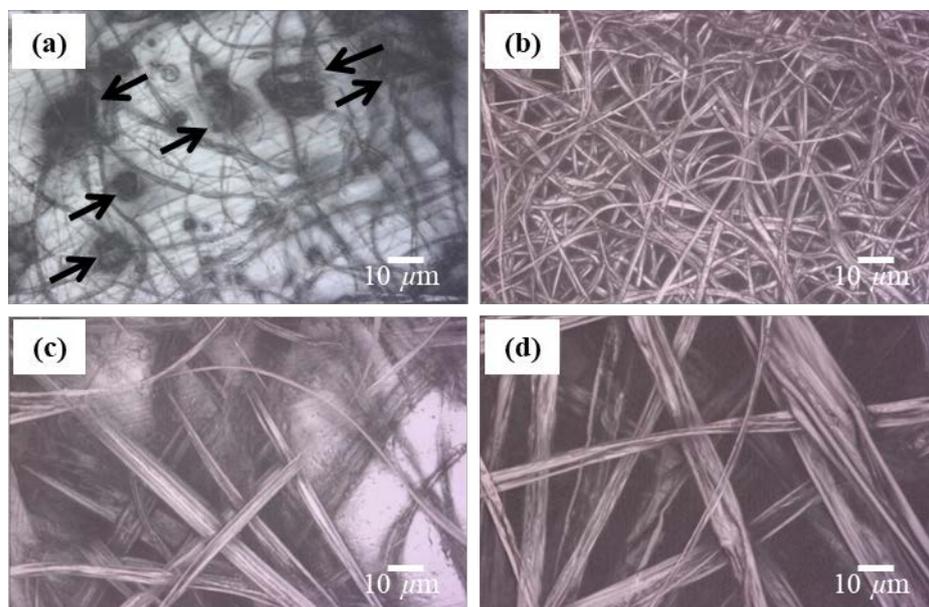
183 organic solvents were prepared and subjected to electrospinning on an aluminum foil-covered iron  
184 collector. As a result, the electrospun fibers were able to be obtained from 11 wt.% and higher  
185 concentrations of WSCA solutions in 40 wt.% aqueous ethanol [Fig. 2(c)–(d)]. However, a  
186 solution of WSCA at 5 wt.% gave only beads, and solutions at 7, and 9 wt.% gave beads and fibers  
187 [Fig. 2(a)–(b)]. The average diameter of electrospun fibers was increased as an increase in WSCA  
188 concentration (Supplementary Table S1). This result was consistent with the previous findings  
189 (Amiraliyan *et al.* 2009, Tarus *et al.* 2016). Therefore, WSCA solution at 11 wt.% in 40 wt.%  
190 aqueous ethanol yielded the finest fibers with an average diameter of 1.20  $\mu\text{m}$  and smooth surface



**Fig. 2.** Morphology of electrospun fibers at 7 wt.% (a), 9 wt.% (b), 11 wt.% (c), and 15 wt.% (d) of WSCA concentrations in 40 wt.% ethanol solution. Arrows indicate droplets and beads.

191 [Fig. 2(c)], and was used for the following experiments to obtain thin fibers.

192 In the case of CDA, the electrospun fibers were obtained from CDA at 90 wt.% aqueous  
193 acetone. CDA solution at 7 wt.% concentration in the aqueous acetone gave both of fibers and



**Fig. 3.** Morphology of electrospun fibers at 7 wt.% (a), 9 wt.% (b), 11 wt.% (c), and 15 wt.% (d) of CDA concentrations in 90 wt.% acetone solution. Arrows indicate droplets and beads.

194 beads [Fig. 3(a)]. Fine fibers were obtained from the solution at 9 wt.% and 15 wt.% [Fig. 3(b)  
195 and (d)], respectively. CDA solution at 9 wt.% yielded the finest fibers among the tested solutions  
196 with an average diameter of 1.69  $\mu\text{m}$  [Fig. 3(b)]. This solution conditions were applied to the  
197 following electrospinning experiments.

#### 198 **Electrospinning and adhesion of CA fibers on PU sheet**

199 Electrospinning of WSCA and CDA on the PU sheets, which were rolled in parallel on  
200 the iron collector, was attempted using the optimized solutions of WSCA and CDA as mentioned  
201 above. Electrospun fibers were deposited on the PU sheets only for initial 2 min. Afterwards, the  
202 fibers were deposited out of the PU sheets, especially, on the non-covered surface of the iron  
203 collector between PU sheets, as shown in Fig. 4 (a) and (b). It was assumed that PU sheets were  
204 an electric insulator, and static charge was accumulated on the sheet during electrospinning,  
205 leading to unsuccessful electrospinning. To remove the static charge, anti-static agent was sprayed  
206 several times on the sheets during electrospinning. By this treatment, both CA fibers were  
207 successfully deposited on the PU sheets [Fig. 4 (c)]. This method of spraying anti-static agent was  
208 applied to other synthetic polymer sheets, such as polyethylene and poly(methylmethacrylate)  
209 sheets. As a result, this spraying method was found to be effective in direct electrospinning of CA  
210 fibers on any synthetic polymer sheet.

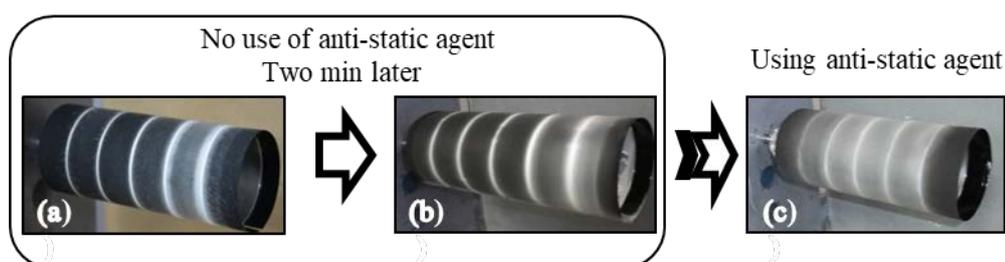
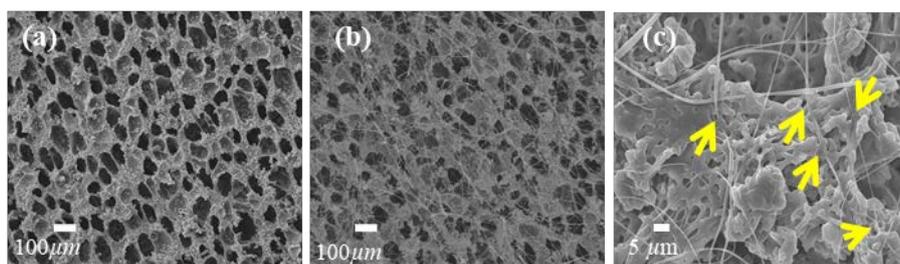


Fig. 4 Electrospun fibers deposited on PU sheet for initial 2 min (a), after 2 min (b), and with an anti-static agent (c).

211 However, another problem arose: the resulting electrospun CA fibers were easily peeled off  
212 from PU sheet by rubbing with a finger [Supplementary Figure S2 (a)]. To estimate the adhesion  
213 strength, fiber peeling was observed under different loads in the tribology test. The resulting  
214 electrospun CA fibers were peeled off from PU sheet under only 5 gf load [Supplementary  
215 Figure S3 (a)]. To overcome this problem, we changed a strategy for fixation of electrospun fibers  
216 on the PU sheets. DMF, as a good solvent for PU and CA, was attempted to be sprayed, in order to  
217 partly dissolve both materials to fuse them. When DMF was directly sprayed to the sheets, the  
218 electrospun fibers on PU sheets were almost dissolved to lose the fiber morphology, suggesting  
219 that DMF should be diluted. Thereby, DMF was diluted with ethanol to several concentrations,  
220 and the DMF solutions were sprayed directly on the fiber deposited PU sheet to check dissolution  
221 and adhesion of CA fibers. From this preliminary experiment, 50 wt.% of DMF/ethanol solution  
222 was found to be a suitable solution (Supplementary Figure S4). However, this spray fixation  
223 gave rise to another problem to give a damage to PU sheet surface. To avoid the problem, the  
224 fiber-deposited PU sheets were dragged in the mist, which was prepared by spraying DMF/ethanol  
225 solution (50 wt.%) for 1 sec  $\times$  3 times into the air. As a result, electrospun fibers were partly fused  
226 with PU sheets (Fig. 5). Electrospun CA fibers after fixation were not peeled off easily from the

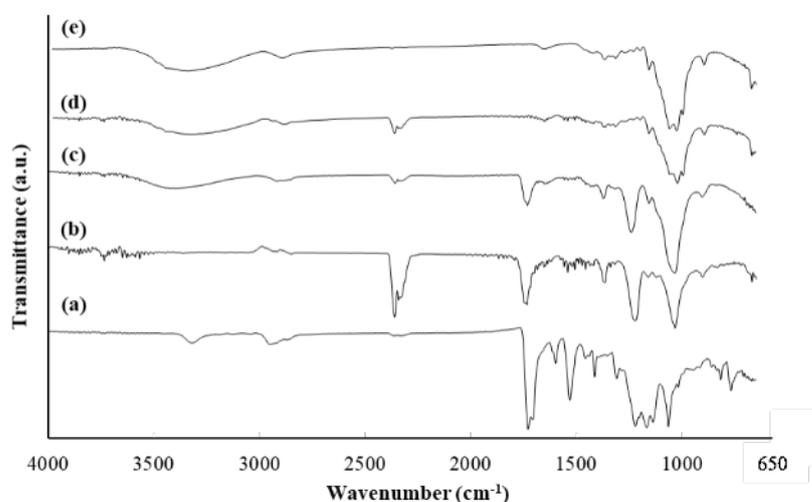
227 PU sheet by rubbing with a finger or even under 150 gf load using tribology test machine  
228 [Supplementary Figures S2 (b) and S3 (b)].



**Fig. 5** SEM images of PU sheet before spinning (a), after spinning (b) and after fixation (c). Arrows indicate fused parts of CA fibers and PU sheet.

### 229 Conversion of CA to regenerated cellulose by saponification

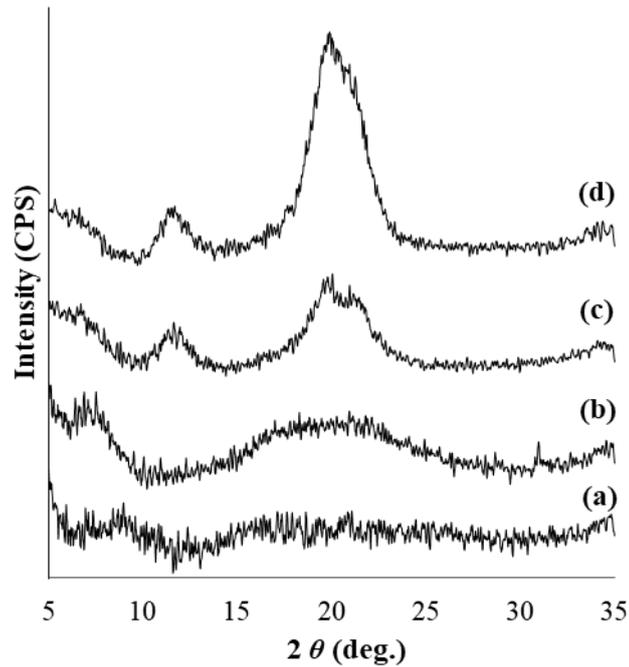
230 CA was saponified with a vapor of 28%  $\text{NH}_3$  aqueous solution to produce regenerated  
231 cellulose (Takahashi *et al.* 2013). The changes in the chemical structure of the CA fibers upon  
232 saponification were analyzed by using an ATR-FTIR. Since PU itself carries carbonyl groups, the  
233 carbonyl band assigned to PU and CA could not be distinguished. Therefore, completion of  
234 saponification was monitored by ATR-FTIR, using WSCA and CDA electrospun fibers deposited  
235 on aluminum foil. In **Fig. 6**, an ester carbonyl band at  $1745\text{ cm}^{-1}$  was clearly observed in the  
236 spectra of WSCA and CDA electrospun fibers. The carbonyl band disappeared upon the  
237 saponification for 7 d, indicating that both CAs were converted completely to regenerated  
238 cellulose.



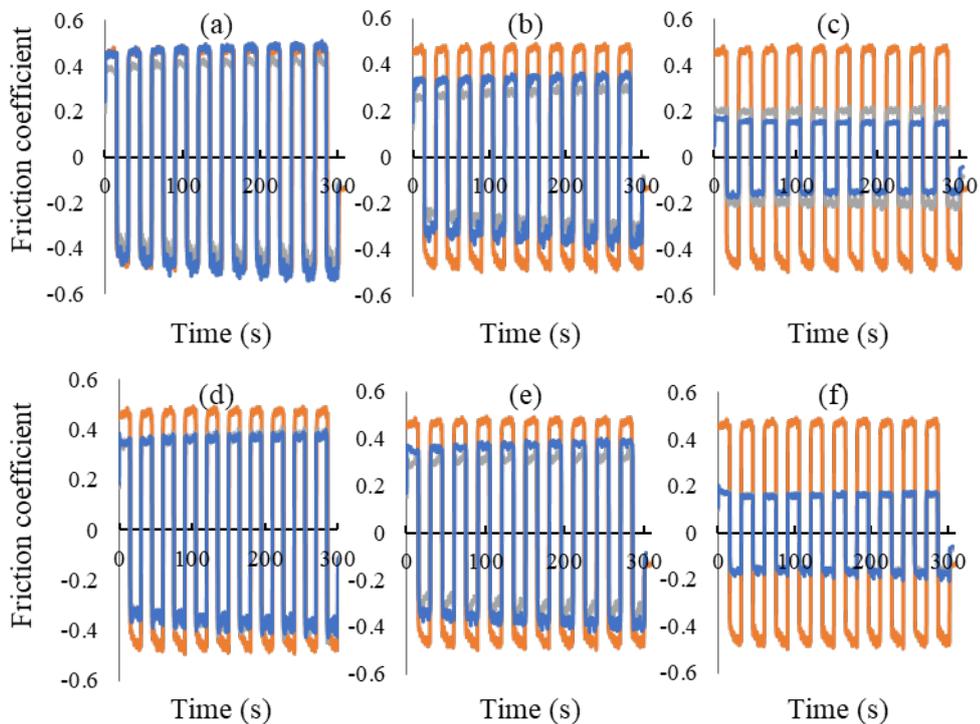
**Fig.6.** ATR-FTIR spectra of PU sheet (a), CDA fibers (b), WSCA fibers (c), saponified CDA fibers (d) and saponified WSCA fibers (e).

239 X-ray diffraction (XRD) of electrospun CA fibers before and after saponification was  
240 measured to elucidate crystalline structure (**Fig. 7**). Broad peaks at less than  $10^\circ$  and at around  $20^\circ$   
241 were observed in unsaponified WSCA and CDA electrospun fibers [**Fig. 7 (a) and (b)**], indicating  
242 these fibers were amorphous. Saponified CDA fibers showed sharp peaks at  $2\theta = 11.6^\circ$ ,  $20.1^\circ$ , and  
243  $21.2^\circ$ , although each intensity was not so high, suggesting a crystalline structure of cellulose II  
244 polymorph [**Fig. 7 (c)**]. However, saponified WSCA fibers showed peaks at  $2\theta = 11.9^\circ$  and  $20.0^\circ$ ,  
245 where two peaks at  $20.1^\circ$ , and  $21.3^\circ$  might be overlapped [**Fig. 7 (d)**]. This observation suggested

246 that CDA gave the regenerated cellulose with higher crystallinity. Thus, this saponification with  
 247  $\text{NH}_3$  vapor brought about not only deacetylation but also crystallization.



**Fig. 7.** X-ray diffractograms of WSCA fibers (a), CDA fibers (b), regenerated cellulose from CDA fibers (c), and regenerated cellulose from WSCA fibers (d).



**Fig. 8.** Profiles of friction coefficient under a load of 150 gf in the tribology test. (a)-(c), intact PU sheets (orange line), WSCA fibers (gray line), saponified WSCA fibers (blue line) deposited on PU sheets. (d)-(f), intact PU sheets (orange line), CDA fibers (gray line) and saponified CDA fibers (blue line) deposited on PU sheets. (a) and (d), at the deposited fiber amount of  $0.81 \text{ g/m}^2$ ; (b) and (e), at the deposited fiber amount of  $1.61 \text{ g/m}^2$ ; (c) and (f), at the deposited fiber amount of  $3.20 \text{ g/m}^2$ .

248 **Tribology test of surface modified PU sheets**

249 Tribology test was carried out to evaluate the change in physical property of PU sheets  
 250 upon the electrospun fibers deposition and saponification. Amounts of both WSCA and CDA  
 251 electrospun fibers deposited on PU sheets were 0.81, 1.61 and 3.20 mg/m<sup>2</sup>. Tribology test was  
 252 carried out under the loads of 50, 100, and 150 gf. Profiles of friction coefficients for CA-  
 253 deposited PU sheet under the load of 150 gf in the tribology test are typically shown in **Fig. 8**,  
 254 because other profiles under any loads were found very similar. The static ( $\mu_s$ ) and the kinetic ( $\mu_k$ )  
 255 friction coefficients are summarized in **Table 1**. Both coefficients of PU sheet were decreased by  
 256 the deposition of WSCA and CDA fibers, and the decrement of coefficients depended on the  
 257 deposited amounts of fibers. This phenomenon can be explained as follows. The friction  
 258 coefficient of intact PU sheet was high probably due to the rough surface. When CA fibers were  
 259 deposited on the PU sheet, the rough surface was partially covered with the fibers. As a result, the  
 260 surface became flat, leading to a decrease in friction coefficients and its dependency on deposited

**Table 1.** Friction coefficient of intact PU sheet, CDA and WSCA electrospun fibers-deposited on PU sheet, and their saponified fibers-deposited PU sheet with varying amounts of deposited fibers under different loads (50, 100 and 150 gf).

Friction coefficient	PU sheet	Fiber amount 0.81 mg /m <sup>2</sup>				Fiber amount 1.61 mg /m <sup>2</sup>				Fiber amount 3.20 mg /m <sup>2</sup>			
		WSCA		CDA		WSCA		CDA		WSCA		CDA	
		Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>
<b>Load : 50 gf</b>													
$\mu_s$	0.560	0.418	0.515	0.322	0.387	0.269	0.334	0.323	0.355	0.172	0.155	0.154	0.174
$\mu_k$	0.564	0.411	0.502	0.315	0.367	0.248	0.378	0.315	0.357	0.166	0.149	0.149	0.170
<b>Load : 100 gf</b>													
$\mu_s$	0.507	0.430	0.499	0.370	0.409	0.290	0.365	0.349	0.391	0.205	0.154	0.164	0.181
$\mu_k$	0.509	0.423	0.489	0.352	0.389	0.275	0.356	0.332	0.371	0.195	0.147	0.159	0.176
<b>Load : 150 gf</b>													
$\mu_s$	0.444	0.409	0.483	0.395	0.394	0.301	0.338	0.342	0.380	0.206	0.157	0.163	0.168
$\mu_k$	0.459	0.409	0.475	0.365	0.365	0.279	0.338	0.316	0.366	0.202	0.152	0.160	0.163

$\mu_s$  and  $\mu_k$  are static friction coefficient and kinetic friction coefficient, respectively.

<sup>a</sup> Before saponification. <sup>b</sup> After saponification.

Moving speed of aluminum ball: 2 mm/sec, Distance: 30 mm, Reciprocation: 10 times

261 amounts of fibers.

262 By saponification, all the friction coefficients were increased, except for those of WSCA-  
 263 deposited PU sheet at the amount of 3.20 mg/m<sup>2</sup>. This phenomenon was explained by the change  
 264 in both types of CA fiber structure from amorphous state before saponification to crystalline state  
 265 after saponification, as shown in **Fig. 7**. The deposited crystalline fibers might have high Young's  
 266 modulus or high stiffness that directly affected the friction coefficients.

267 In the case of saponified WSCA fibers deposited on PU sheets at 0.81 and 1.61 mg/m<sup>2</sup>,  
 268 the friction coefficients had a similar trend to those of saponified CDA fibers, while the friction  
 269 coefficients of saponified WSCA fibers at 3.20 mg/m<sup>2</sup> was lower than those of non-saponified  
 270 ones and was the lowest among samples. Although the reason for the lowest coefficients is unclear,  
 271 the thickness or the diameter of the electrospun fibers may affect the friction coefficients. The  
 272 saponified WSCA electrospun fibers (1.16  $\mu\text{m}$  in diameter) were thinner than the corresponding  
 273 CDA fibers (1.73  $\mu\text{m}$  in diameter). When much larger amount of fine CA fibers was deposited on  
 274 the PU sheet, the rough surface of the sheet was considered to be densely covered with the fibers

275 to give flatter surface or to decrease surface roughness. The smaller surface roughness of the  
276 WSCA fibers (3.20 mg/m<sup>2</sup>)-deposited PU sheet was confirmed by 3-D laser microscopic  
277 observation, according to ISO 4287: 1997 (**Supplementary Table S2**). The flatter surface would  
278 give lower resistance to the friction against an aluminum ball as a probe of this tribology  
279 measurement. Thus, the surface physical property of PU sheets was found to be dramatically  
280 altered by the deposition of WSCA and CDA electrospun fibers and their saponification.

## 281 **Conclusion**

282 Modification of surface physical property of PU sheet was attempted by direct electrospinning  
283 of WSCA and CDA solutions in this study. Fine electrospun fibers with diameters of 1.20  $\mu\text{m}$  and  
284 1.69  $\mu\text{m}$  were obtained from 11 wt.% of WSCA in 40 wt.% aqueous ethanol solution and 9  
285 wt.% of CDA in 90 wt.% aqueous acetone solution, respectively. Direct electrospinning of both  
286 CA fibers on non-electroconductive PU sheets was successfully carried out by spraying an anti-  
287 static agent on PU sheet to remove the static charge. This method of spraying an anti-static agent  
288 enabled direct electrospinning of CA on any types of synthetic polymer sheet, such as  
289 polyethylene and poly(methylmethacrylate).

290 Although the deposited fibers on PU sheet were easily peeled off from PU sheet by finger  
291 rubbing, the fibers were tightly fixed on the sheet by dragging the fiber-deposited PU sheets in the  
292 mist of DMF/ethanol solution followed by partial fusion of the fibers with the surface of PU sheet.  
293 The WSCA and CDA electrospun fibers were saponified with NH<sub>3</sub> vapor to yield regenerated  
294 cellulose fibers with obvious crystalline structure of cellulose II polymorph. In tribology test, the  
295 friction coefficients of electrospun CA fibers-deposited PU sheet were decreased with an increase  
296 in the amount of CA deposited. Moreover, the friction coefficients of the sheet were slightly  
297 increased by saponification, except for WSCA fibers-deposited PU sheet at 3.20 mg/m<sup>2</sup>. Thus,  
298 surface physical property of PU sheet was successfully altered by direct electrospinning of CAs  
299 and their saponification.

300

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