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Direct Electrospinning of Cellulose Acetate onto Polyurethane Sheet and Effect of Its Saponification on Mechanical Properties

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Abstract

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

Keywords: Electrospinning · Cellulose acetate · Surface modification · Saponification· Regenerated cellulose · Tribology test

Introduction

Cellulosic materials, cellulose nanofiber (CNF) (Yano *et al*., 2005; Ito, 2013; Kakroodi *et al*., 2014; Wang *et al*., 2014), and other cellulosics including 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.

There are two possible methods proposed; solution coating and direct deposition of solid material for the surface modification of plastics with cellulosics. 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 cellulosic onto plastics is possible, this method must bring the high elasticity to plastic surface.

A concept of electrospinning was proposed in the 16th 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; Kongkhlang *et al*., 2008; Nicosia *et al*., 2016). Cellulose derivatives, for example, cellulose acetate (CA), which dissolves in

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

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

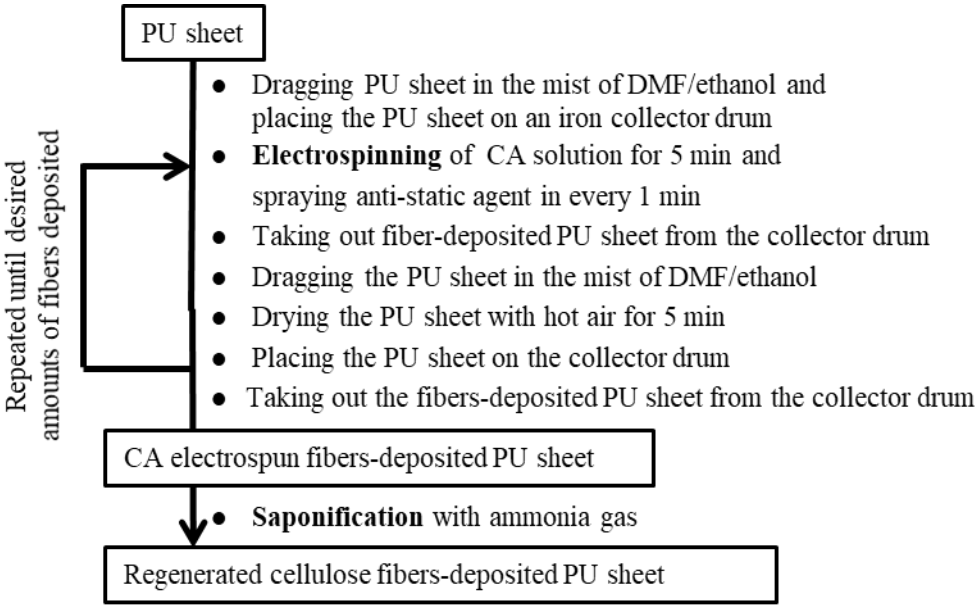

Fig. 1. Preparation strategy of regenerated cellulose fibers-deposited PU sheet.

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

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

Experiment

Materials

Water-soluble cellulose acetate (WSCA) with a degree of substitution (DS) of 0.9 and cellulose di-acetate (CDA) with a DS of 2.4 were kindly supplied from Daicel Corporation, Ltd., (Osaka, Japan). DMF, acetone, ethanol, acetic acid and aqueous NH_3 (28%) were purchased from Wako Pure Chemical Ltd., (Tokyo, Japan). An anti-static agent (staticide: 99.8% of anhydrous isopropyl alcohol) was purchased from ACL Inc. (Chicago, IL, U.S.A.). Fifty to 90 wt.% DMF/ethanol solutions were prepared. As a polishing agent for compact disc (CD) and hard disc (HD), polyurethane (PU) sheet with poly(ethylene terephthalate) (PET) as a supporting film was provided from Fujibo Ehime Co., Ltd. (Saijo, Japan) **(Supplementary Figure S1).** Stainless steel plate for tribology measurement was purchased from Yamamoto-MS Co., Ltd. (Tokyo, Japan).

Electrospinning

Simple electrospinning of WSCA and CDA on aluminum foil and PU sheet

WSCA was dissolved at 50 ^{o}C in 40 wt.% aqueous ethanol solution to give its solutions at concentrations of 1-17 wt.%. CDA was dissolved in 90 wt.% aqueous acetone solution to give its solutions at concentrations of 1-17 wt.%.

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

Preparation of electrospun CA fibers fixed on PU sheet

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

Saponification of CA fibers

The CA fiber-deposited PU sheet was cut into pieces (about 6 × 3.79 cm^2), and the resultant PU sheets were placed in a petri-dish (9 cm in diameter). About 50 mL of 28% NH_3 aqueous solution was poured into another petri-dish (9 cm in diameter). Both petri-dishes were placed in a large petri-dish (20 cm in diameter). Top of the large dish was covered with another large dish, and this set of petri-dishes was sealed with para-film and cooking wrap. The dish-set was left standing for one week at room temperature. The PU sheets were then taken out of the petri-dish and washed with distilled water. The PU sheets were dried *in vacuo* overnight at room temperature.

Tribology test

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

Instrumental analysis

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

Results and discussion

Electrospinning of WSCA and CDA

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

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

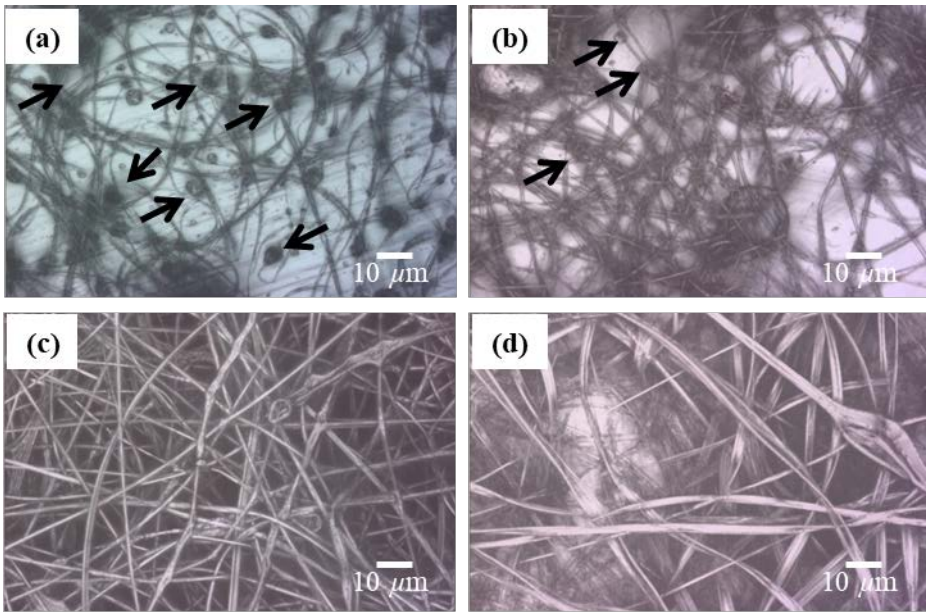

Fig. 2. Morphology of electrospun fibers at 7 wt.% (a), 9 wt.% (b), 11 wt.% (c), and 15 wt.% (d) of WSCA concentrations in 40 wt.% ethanol solution. Arrows indicate droplets and beads.

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

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

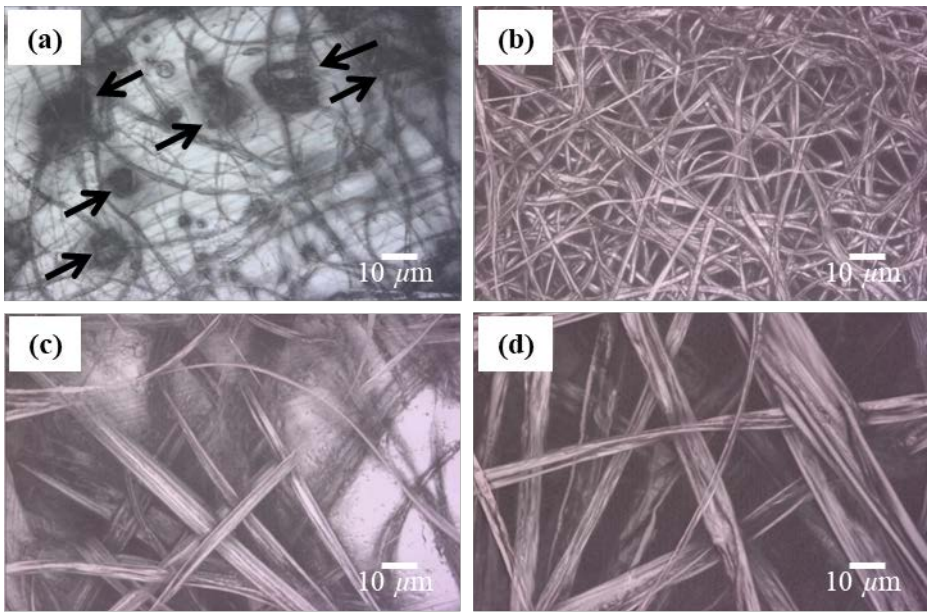

Fig. 3. Morphology of electrospun fibers at 7 wt.% (a), 9 wt.% (b), 11 wt.% (c), and 15 wt.% (d) of CDA concentrations in 90 wt.% acetone solution. Arrows indicate droplets and beads.

beads **[Fig. 3(a)]**. Fine fibers were obtained from the solution at 9 wt.% and 15 wt.% **[Fig. 3(b) and (d)]**, respectively. CDA solution at 9 wt.% yielded the finest fibers among the tested solutions with an average diameter of 1.69 μm **[Fig. 3(b)]**. This solution conditions were applied to the following electrospinning experiments.

Electrospinning and adhesion of CA fibers on PU sheet

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

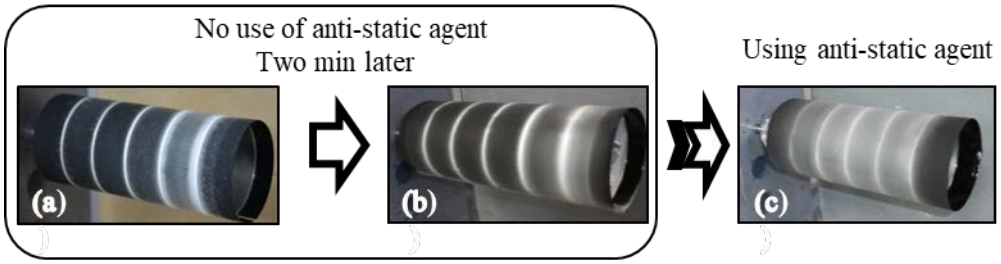

Fig. 4 Electrospun fibers deposited on PU sheet for initial 2 min (a), after 2 min (b), and with an anti-static agent (c).

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

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

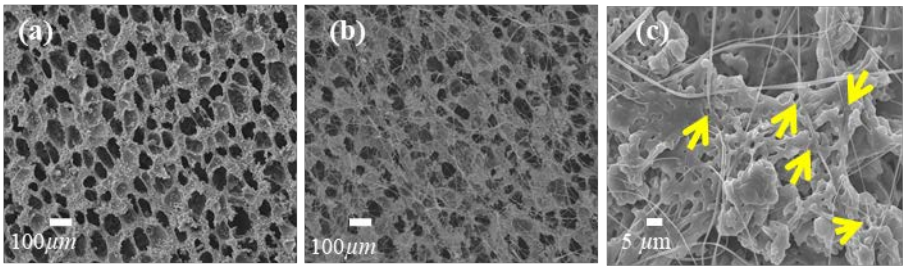

Fig. 5 SEM images of PU sheet before spinning (a), after spinning (b) and after fixation (c). Arrows indicate fused parts of CA fibers and PU sheet.

Conversion of CA to regenerated cellulose by saponification

CA was saponified with a vapor of 28% NH_3 aqueous solution to produce regenerated cellulose (Takahashi *et al.* 2013). The changes in the chemical structure of the CA fibers upon saponification were analyzed by using an ATR-FTIR. Since PU itself carries carbonyl groups, the carbonyl band assigned to PU and CA could not be distinguished. Therefore, completion of saponification was monitored by ATR-FTIR, using WSCA and CDA electrospun fibers deposited on aluminum foil. In **Fig. 6**, an ester carbonyl band at 1745 cm^{-1} was clearly observed in the spectra of WSCA and CDA electrospun fibers. The carbonyl band disappeared upon the saponification for 7 d, indicating that both CAs were converted completely to regenerated cellulose.

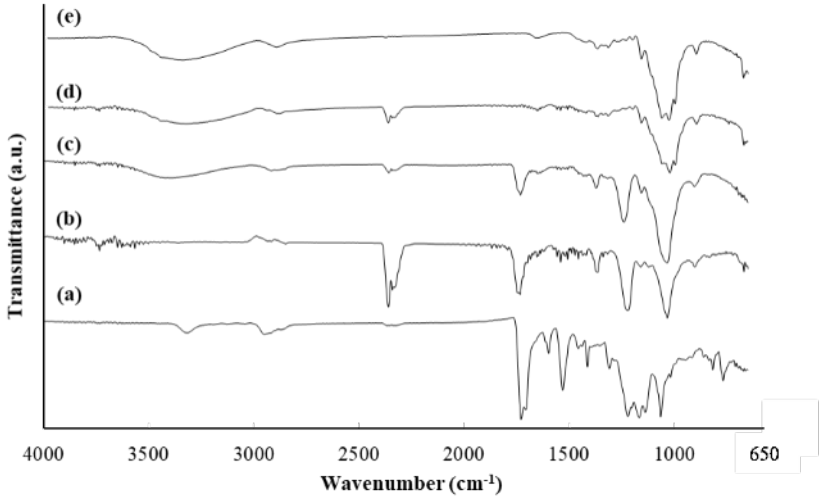

Fig.6. ATR-FTIR spectra of PU sheet (a), CDA fibers (b), WSCA fibers (c), saponified CDA fibers (d) and saponified WSCA fibers (e).

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

246 that CDA gave the regenerated cellulose with higher crystallinity. Thus, this saponification with
247 NH_3 vapor brought about not only deacetylation but also crystallization.

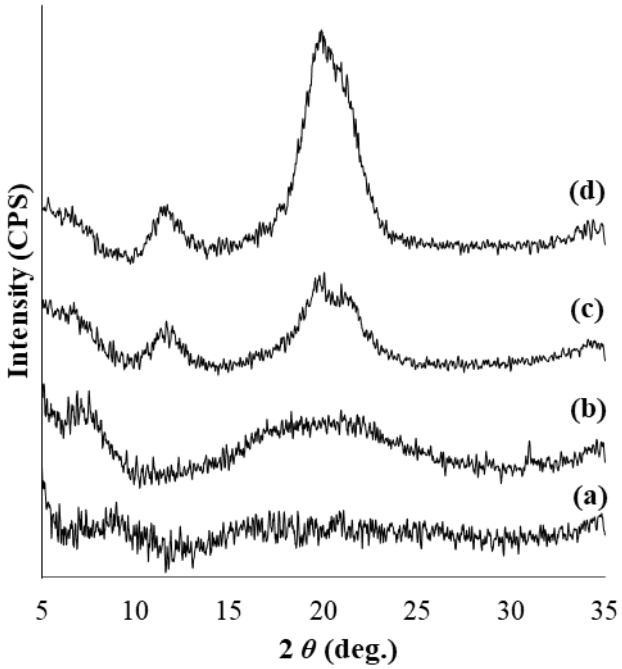

Fig.7. X-ray diffractograms of WSCA fibers (a), CDA fibers (b), regenerated cellulose from CDA fibers (c), and regenerated cellulose from WSCA fibers (d).

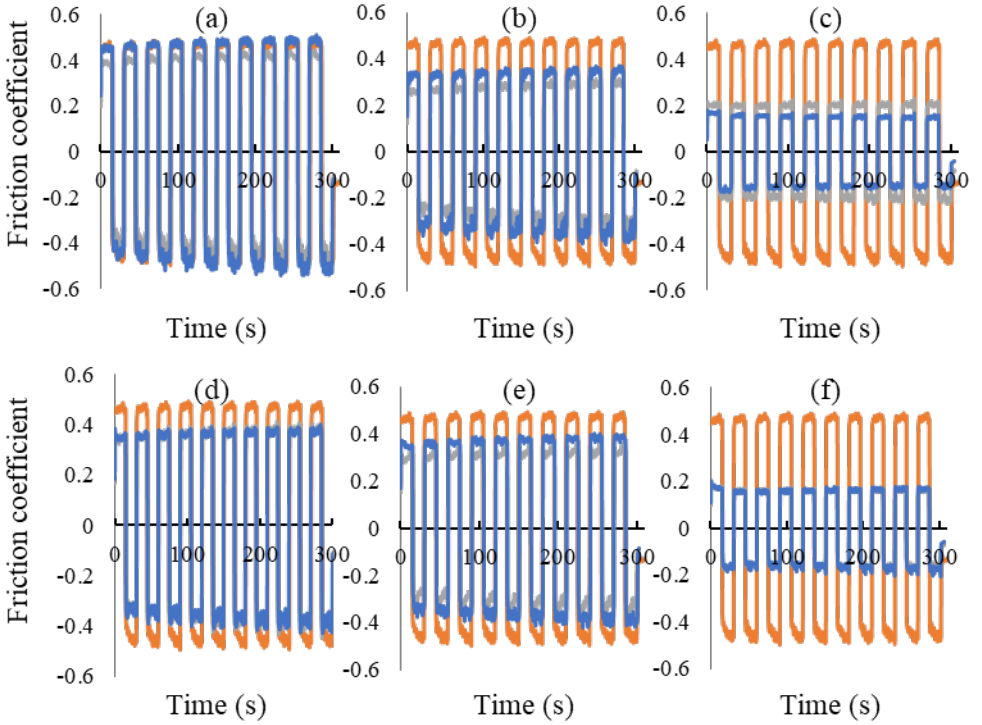

Fig. 8. Profiles of friction coefficient under a load of 150 gf in the tribology test. (a)-(c), intact PU sheets (orange line), WSCA fibers (gray line), saponified WSCA fibers (blue line) deposited on PU sheets. (d)–(f), intact PU sheets (orange line), CDA fibers (gray line) and saponified CDA fibers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

Tribology test of surface modified PU sheets

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

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^2				Fiber amount 1.61 mg /m^2				Fiber amount 3.20 mg /m^2			
		WSCA		CDA		WSCA		CDA		WSCA		CDA	
		Before[a]	After[b]	Before[a]	After[b]	Before[a]	After[b]	Before[a]	After[b]	Before[a]	After[b]	Before[a]	After[b]
Load : 50 gf													
μ_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
μ_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
Load : 100 gf													
μ_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
μ_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
Load : 150 gf													
μ_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
μ_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

μ_s and μ_k are static friction coefficient and kinetic friction coefficient, respectively.
[a] Before saponification. [b] After saponification.
Moving speed of aluminum ball: 2 mm/sec, Distance: 30 mm, Reciprocation: 10 times

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

In the case of saponified WSCA fibers deposited on PU sheets at 0.81 and 1.61 mg/m^2, the friction coefficients had a similar trend to those of saponified CDA fibers, while the friction coefficients of saponified WSCA fibers at 3.20 mg/m^2 was lower than those of non-saponified ones and was the lowest among samples. Although the reason for the lowest coefficients is unclear, the thickness or the diameter of the electrospun fibers may affect the friction coefficients. The saponified WSCA electrospun fibers (1.16 μm in diameter) were thinner than the corresponding CDA fibers (1.73 μm in diameter). When much larger amount of fine CA fibers was deposited on the PU sheet, the rough surface of the sheet was considered to be densely covered with the fibers

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

Conclusion

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

Although the deposited fibers on PU sheet were easily peeled off from PU sheet by finger rubbing, the fibers were tightly fixed on the sheet by dragging the fiber-deposited PU sheets in the mist of DMF/ethanol solution followed by partial fusion of the fibers with the surface of PU sheet. The WSCA and CDA electrospun fibers were saponified with NH_3 vapor to yield regenerated cellulose fibers with obvious crystalline structure of cellulose II polymorph. In tribology test, the friction coefficients of electrospun CA fibers-deposited PU sheet were decreased with an increase in the amount of CA deposited. Moreover, the friction coefficients of the sheet were slightly increased by saponification, except for WSCA fibers-deposited PU sheet at 3.20 mg/m^2. Thus, surface physical property of PU sheet was successfully altered by direct electrospinning of CAs and their saponification.

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