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Modification of cellulose nanofibre surfaces by He/NH₃ plasma at atmospheric pressure

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Abstract: Cellulose nanofibre coatings were treated by a dielectric barrier discharge plasma in a He/NH₃ gas mixture at atmospheric pressure. Ultrasound was optionally irradiated during the treatment. The treatment enhanced the wetting of deionized water, glycerol, and uncured epoxy. Irradiation of ultrasound did not significantly change optical emission from the plasma, but increased the oxygen contents and enhanced etching and roughening at the nanofibre coating surfaces. Furthermore, the irradiation of ultrasound enhanced the wetting of deionized water and glycerol drastically, while that of uncured epoxy to some extent.

cellulose; nanofibre; plasma treatment; dielectric barrier discharge; ultrasound; wetting; surface roughening

Introduction

Cellulose nanofibres (CNFs) attract significant interests due to their mechanical and optical properties (Peng et al. 2011), and are applied in packaging (Herrera et al. 2014, 2016), rheology modifiers (Becker 2018), sporting goods (Matsuda 2015), automotive (Wikström 2017), and aeronautical industries (Wikström 2017). The mechanical properties of CNFs can be optimally used when the CNFs interact to a polymer matrix at the interface to achieve strong, lightweight composites (Nakagaito and Yano 2005). Therefore, improving the interaction at the interface by modification of CNF surfaces is important (Siró et al. 2013). Among surface modification techniques reported, plasma treatment is promising due to no need of solvent and environmental compatibility with high efficiency

(Strobel et al. 1994). A plasma is an ionized gas. It contains reactive species including electrons, ions, and radicals, usually accompanying an ultraviolet emission. Plasma treatment is carried out by exposing a material surface in such a reactive environment. Such plasmas can be generated and operated at low and atmospheric pressures (Kogoma et al. 2011; Kusano 2014). Atmospheric pressure plasmas are widely used, and the examples include a dielectric barrier discharge (DBD) (Kogelschatz 2003), a corona discharge (Goldman et al. 1985), a cold plasma torch (Mortensen et al. 2006; Schutze et al. 1998, Lee et al. 1997), and a gliding arc (Fridman et al. 1999; Sun et al. 2013; Kusano et al. 2013b, 2014b, 2016). A DBD is among the most widely used atmospheric pressure plasmas. It is driven by an alternating-current (AC) voltage, and generated between electrodes separated by dielectrics. Air-to-air type continuous treatment system can be easily designed due to the simple setup of DBDs (Kusano et al. 2008; Teodoru et al. 2009).

Irradiation of ultrasound can improve treatment effects of atmospheric pressure plasmas. The effect of ultrasound is considered to be thickness reduction of the boundary layer of a gas on a material surface (Kusano 2009; Kusano et al. 2010, 2011a, b, 2012b, 2013a, 2014a, 2015, 2018). Due to the thickness reduction, the reactive species in a plasma can more easily approach the material surface. The enhanced treatment effects are demonstrated for DBDs in helium (Kusano 2014; Kusano et al. 2010, 2012b, 2013a, 2014a, 2018) and air (Kusano et al. 2011b, 2012b), and for a gliding arc in air (Kusano et al. 2011a, 2015). Apart from the enhanced surface modification effects reported, the ultrasonic irradiation can reduce the current pulse width (Kusano et al. 2010, 2013a). However, the profile of the photoemission spectrum does not change significantly (Kusano et al. 2011b), and thus the rotational temperature is almost unchanged by the ultrasonic irradiation (Kusano et al. 2011b, 2013a). Furthermore, it is reported that ozone production in DBDs in oxygen (Drews et al. 2011) and air (Kusano et al. 2012a) is enhanced by ultrasonic irradiation. However, plasmas in no other gas mixtures were investigated with ultrasonic irradiation. Meanwhile, ammonia (NH_3), for example, is often used as a plasma gas for various applications including gas phase reactions (Fateev et al. 2005; Kusano et al. 2005), etching and surface modification (Pringle et al. 1996), and it is interesting to explore the effect of ultrasonic irradiation.

67 In previous works (Kusano et al. 2016, 2018), the effect of He DBD treatment on
68 CNFs was studied. The results show that the He DBD treatment enhanced
69 wettability of deionized water and glycerol, and that ultrasonic irradiation
70 enhanced the effects. However, further improvement of the treatment is desired.
71 In the present work, surface treatment of CNFs was employed by using them in
72 the form of coating to simplify the processes of treatment and characterizations.
73 CNF coatings were subjected to surface treatment using a He/NH₃ DBD plasma
74 with and without ultrasonic irradiation. The static contact angle measurements,
75 field-emission type scanning electron microscopy (FE-SEM), and X-ray
76 photoelectron spectroscopy (XPS) were used for surface characterization before
77 and after the treatment. In addition, plasma diagnostics was performed using
78 optical emission spectroscopy (OES).

79 **Experimental methods**

80 CNFs were taken from carrot residue. CNF suspension was prepared by processes
81 including chemical purification of carrot residue to produce aqueous suspension,
82 dispersion using a shear mixer and subsequent fibrillation. The detailed procedure
83 is described in the previous studies (Kusano et al. 2016, 2018).

84 To prepare the CNF coatings, the CNF suspension was coated on a glass plate
85 (CORNING® 2947-75×25, England), and air-dried in ambient air. The coating
86 thickness is estimated to be 5-10 µm.

87 A DBD plasma was generated and operated using an AC generator (Generator
88 6030, SOFTAL Electronic GmbH, Germany) at atmospheric pressure. A
89 schematic diagram of the DBD setup is illustrated in Figure 1. The grounded
90 bottom electrode (50 mm × 50 mm) was covered with a dielectric plate made of
91 alumina. The powered top electrode had a stainless-steel mesh covering a
92 perforated hole for the ultrasonic introduction (Kusano et al. 2018). Helium at a
93 flowrate of 3 L/min and ammonia at a flowrate of 3 mL/min were premixed and
94 then introduced to the DBD plasma in a 5 mm gap. On the alumina plate the CNF
95 coated glass plate was located to modify the CNF surface.

96 A gas jet ultrasonic generator (SonoSteam; FORCE Technology, Denmark) was
97 used to introduce ultrasonic waves vertically to the CNF coating surface through a
98 waveguide (Kusano 2014; Kusano et al. 2010, 2011a, b, 2012b, 2013a, 2014a,
99 2015, 2018). As a membrane to separate ambient air and plasma gas, polyethylene

100 (PE) film was used in the waveguide. The ultrasound passing the thin PE film and
 101 reaching at the DBD has the sound pressure level of approximately 155 dB
 102 (Kusano et al. 2011b). Here, the ultrasonic emitter is not designed for the specific
 103 DBD, and thus treatment efficiency in terms of energy cannot be discussed in the
 104 present study.
 105

106
 107 Figure 1. The schematic diagram of the DBD plasma setup with an ultrasonic generator.
 108

109 The surface wettability of the CNF coatings was evaluated by measuring the
 110 contact angles (CAM100, Crelab Instruments AB, Sweden) at room temperature
 111 in ambient air. The testing liquids used are deionized water, glycerol, and uncured
 112 epoxy (Araldite LY 1568). These testing liquids are polar liquids. The viscosities
 113 of these three testing liquids at 25°C are 0.89, 1.2, and 1.3-1.5 cP, respectively.
 114 Each point in Figures 4 and 5 corresponds to an average value of each specimen.
 115 The average value was obtained by measuring ten or more individual
 116 measurements for deionized water and glycerol and five or more individual
 117 measurements for the uncured epoxy. Morphologies of the CNF coating surfaces
 118 were observed using FE-SEM (SUPRA 35, Zeiss, Germany). Approximately 15
 119 nm thick Au film was sputter deposited on the CNF coatings to avoid charging
 120 during observation with FE-SEM.
 121 XPS data was collected (K-Alpha, ThermoFisher Scientific, UK) and the atomic
 122 composition at the measured surfaces was calculated. In addition a regional
 123 analyses of the carbon 1s (C1s) and nitrogen 1s (N1s) spectra were carried out.

124 The full-width at half-maximum of the peaks for C1s and N1s was fixed at 1.5
125 eV.

126 For the identification of excited species in the DBD plasma, optical emission
127 spectroscopy (OES) was carried out without a specimen using an optical fibre and
128 a spectrometer (PI-MAX 1024, Princeton Instruments, USA) in a range of the
129 wavelength between 280 and 400 nm.

130 **Results and discussion**

131 Interfacial interaction between reinforcement and a polymer matrix is important
132 for overall properties, in particular mechanical properties of composites (Akovali
133 1993). Surface morphology plays an important role in the interaction, since larger
134 surface unevenness usually corresponds to a larger surface area, leading to a larger
135 contact area at the interfaces in the composites. FE-SEM was used to observe how
136 the DBD treatment can affect the CNF coating surfaces at different plasma powers
137 and treatment times. Figure 2 illustrates the FE-SEM images of an untreated CNF
138 coating and treated ones with the He/NH₃ DBD at a fixed treatment time of 30 s
139 with various plasma powers. Nano-fibres with a diameter of 10-20 nm are
140 observed on the untreated CNF coating surface (Figure 2 (a)). After the DBD
141 treatment without irradiation of ultrasound, nano sized holes were created by
142 plasma-chemical etching, and the number of them moderately increased as the
143 plasma power increases (Figure 2 (b_1-d_1)). Irradiation of ultrasound during the
144 DBD treatment significantly improved the effect of the etching as shown in Figure
145 2 (b_2-d_2).

146

Figure 2. Images of CNF coatings taken by FE-SEM: untreated (a), plasma treated ((b_1) 40 W, (c_1) 60 W, and (d_1) 80 W), and plasma treated ((b_2) 40 W, (c_2) 60 W, and (d_2) 80 W) with ultrasonic irradiation. The treatment time was fixed at 30 s.

When the plasma power was fixed at 60 W and the treatment time was varied, the etching proceeded as the treatment time increased (Figure 3 (a_1-d_1)). Again, when ultrasound is irradiated, the etching was enhanced (Figure 3 (a_2-d_2)). It is noted that the He/NH₃ DBD plasma with ultrasonic irradiation can demonstrate significant chemical etching even at low power of 40 W (Figure 2 (b_2)) or short treatment time of 7 s (Figure 3 (a_2)).

Figure 3. FE-SEM images of plasma treated CNF coatings: treatment time of 7 s (a_1), 15 s (b_1), 30 s (c_1), and 60 s (d_1) at a plasma power of 60 W, and treatment time of 7 s (a_2), 15 s (b_2), 30 s (c_2), and 60 s (d_2) at a plasma power of 60 W with the ultrasonic irradiation.

Figures 4 and 5 show the contact angles before and after the He/NH₃ DBD treatment of the CNF coatings at a fixed treatment time of 30 s with various plasma powers, and at various treatment times with a fixed plasma power at 60 W, respectively. They correspond to the conditions in Figures 2 and 3, respectively. The contact angle of water for the untreated CNF coating was approximately 30°, and it decreased to below 20° after the treatment. The irradiation of ultrasound further lowered the water contact angle. In the previous work with He DBD plasma treatment, the water contact angle was rather insensitive against the plasma power (Kusano et al. 2018). However, in the present work with using a

173 He/NH₃ gas mixture, the water contact angle tends to decrease at higher plasma
 174 power or longer treatment time.

175

176

177 Figure 4. Contact angles on CNF coatings, untreated ones plotted at 0 W and after DBD treatment
 178 for 30 s at varying plasma power with (open) and without (solid) irradiation of ultrasound. Testing
 179 liquids: deionized water (triangle), glycerol (circle), and epoxy (star).

180

181

182 Figure 5. Contact angles on CNF coatings, untreated ones plotted at 0 s and after DBD treatment at
 183 fixed power of 60 W for varying treatment time with (open) and without (solid) irradiation of
 184 ultrasound. Testing liquids: deionized water (triangle), glycerol (circle), and epoxy (star).

185

186 When glycerol was used as a testing liquid, the contact angle of the untreated
 187 CNF coating was about 80°, which decreased to lower than 60° after the treatment.
 188 Irradiation of ultrasound further decreased the glycerol contact angle. On the other
 189 hand, increasing plasma power did not significantly change the glycerol contact
 190 angle. In addition, increasing treatment time did not noticeably affect the wetting
 191 of glycerol. Here, the improvement of wetting by glycerol will likely improve the
 192 process-ability and mechanical properties of manufactured CNF polymer

193 composites. It is because CNF dispersion in an organic solvent is usually used for
194 mixing into a polymer in composite manufacturing process (Herrera et al. 2015).
195 As an example of a practically used polymer matrix, uncured epoxy was used as a
196 testing liquid. The epoxy contact angle of the untreated CNF coating was
197 approximately 45°, and decreased to approximately 30° after the DBD treatment.
198 Irradiation of ultrasound also further decreased the epoxy contact angle to some
199 extent. On the other hand, effects of varying plasma power or varying treatment
200 time are not clearly seen. Improvement of epoxy wetting indicates enhanced
201 interaction of the CNFs to the polymer, most likely leading to improved
202 mechanical strength of subsequent composites.

203 XPS was measured to analyze the atomic composition of the CNF coating
204 surfaces, untreated and after the He/NH₃ DBD treatment. The results of the
205 measured atomic compositions from the survey XPS are listed in Table 1. The
206 content of oxygen increased from approximately 36 at.% to 39-41 at.% after the
207 He/NH₃ DBD treatment. The irradiation of ultrasound consistently increased the
208 oxygen content to 42-43 at.%. The level of the oxidation by the He/NH₃ DBD
209 plasma with and without irradiation of ultrasound is comparable to that by the He
210 DBD with and without irradiation of ultrasound (Kusano et al. 2018). Less than 2
211 at.% of calcium was detected on the untreated surface. Plasma treatment tended to
212 increase the calcium content up to approximately 6 at.%. The increase in the
213 content of calcium can be due to selective etching of the organic materials in the
214 CNF coatings. The treatment time and the plasma power did not significantly
215 affect the oxidation of the CNF coating surfaces.

216 Table 1 summarizes analysis of C1s spectra to study the oxygen containing
217 groups. DBD treatment at 40 W decreased the content of C-C and C-H content,
218 and increased the contents of C-O (CO single bond) and C=O (CO double bond,
219 carbonyl). Increasing plasma power resulted in increase of the C-O content both
220 with and without irradiation of ultrasound. However, longer treatment tended to
221 decrease the C-O content. Increasing plasma power or longer treatment did not
222 significantly change the C=O content, except at the highest plasma power or the
223 longest treatment time with ultrasonic irradiation.

224
225

Table 1. Surface composition and C1s regional analysis of the CNF coatings after plasma treatment.

Time [s]	Power [W]	Ultra- sound	Elemental composition [at.%]					C1s [%]		
			C	O	N	Ca	Si	C-C and C-H	C-O	C=O
0	0	-	61.8	36.1	0.2	1.8	0.0	39	46	15
30	40	-	54.4	40.0	2.3	3.0	0.3	31	48	21
30	60	-	52.5	40.7	2.4	2.6	1.8	27	52	21
30	80	-	55.0	38.9	3.4	2.6	0.0	26	54	20
30	40	√	54.4	42.8	0.5	2.3	0.0	27	51	22
30	60	√	52.1	42.6	0.8	2.3	2.2	28	52	20
30	80	√	52.0	42.2	2.8	3.0	0.0	18	56	26
7	60	-	52.0	40.6	2.9	2.3	2.3	26	53	21
15	60	-	51.0	41.0	2.5	2.4	3.0	27	53	20
60	60	-	53.8	40.6	1.9	3.7	0.0	29	49	22
7	60	√	55.0	42.9	0.0	2.2	0.0	16	63	21
15	60	√	51.3	42.8	3.8	1.9	0.3	19	61	20
60	60	√	48.2	43.1	2.6	6.1	0.0	28	43	29

Figure 6 shows typical N1s spectra of the untreated and plasma-treated CNF coatings. As already listed in Table 1, the nitrogen content of the untreated CNF coating was only less than 1at.%. The resulting N1s spectrum is embedded in a scattering signal as illustrated in Figure 6 (a). After the DBD treatment without ultrasonic irradiation, a broad peak centring at approximately 400 eV is observed (Figure 6 (b)), which can be de-convoluted to two peaks at approximately 399 eV (A) and approximately 401 eV (B), corresponding to $-NH_x$ and $-C=N-OH$, respectively.

238

239 Figure 6. Typical N1s spectra of the CNF coating surfaces. (a). untreated. (b). plasma treated, and
 240 (c). plasma with ultrasonic irradiation.

241

242 When ultrasound was irradiated, in addition to the broad peak at approximately
 243 400 eV (A and B), a peak at approximately 407 eV (C) corresponding to $-C-ONO$
 244 was observed. Therefore, the He/ NH_3 DBD treatment can add a small amount of

nitrogen containing groups on the CNF surfaces, and irradiation of ultrasound can oxidize the nitrogen containing functional group, forming the -C-ONO group. Since it is a highly polar functional group, ultrasonic irradiation might further enhance the interaction with a polymer matrix when a CNF composite is manufactured, if the uncured polymer matrix has a polar nature. Taking account of the FE-SEM observation in Figures 2 and 3, and the XPS results in Table 1 and Figure 6, it is interesting to consider the difference in wetting performances for the three testing liquids, especially when these liquids have a polar nature. One possible explanation for the different wetting performances of these liquids in Figures 4 and 5 is that they can be at least partly attributed to the differences of viscosities. Here the viscosity of water is much lower than those of glycerol and the uncured epoxy. It is suggested that testing liquid with lower viscosity would be more sensitive to the surface morphology, and thus water contact angle varied most significantly at higher power or longer treatment, linked to the change of the morphology. It is therefore expected that glycerol or uncured epoxy would show a similar trend to deionized water if sufficiently long time interval is taken for the contact angle measurement so that the testing liquids have enough time to spread, or if temperature is increased to reduce the viscosity. Finally OES was performed to identify activated species in the plasma as shown in Figure 7. The OES was dominated by the emission from N₂ (Laux et al. 2003). Ultrasonic irradiation did not significantly change the OES, showing good agreement with previous works using a DBD in He (Kusano et al. 2013a) and in air (Kusano et al. 2011b). The OES detects photo-emission from a bulk plasma while the effect of the ultrasound is expected at around the boundary between the bulk plasma and solid surfaces such as the upper electrode or the dielectrics. This can be a reason why no significant difference in OES was observed with or without ultrasonic irradiation in Figure 7. In addition, the emission from NH was not detected. Since NH_x groups were detected on the plasma treated surfaces, it is possible that the emission from NH may be too weak compared to the N₂ emissions.

Figure 7. OES of the He/NH₃ DBD with (red) and without (black) irradiation of ultrasound.

Conclusions

He/NH₃ DBD treatment enhanced oxidation and the wettability on the CNF coatings by polar liquids such as deionized water, glycerol, and uncured epoxy. Irradiation of ultrasound noticeably enhanced the surface roughness by etching. It is expected that the interaction between CNFs and a general organic solvent can be enhanced by the said surface modification, and thus the He/NH₃ DBD treatment at atmospheric pressure with irradiation of ultrasound is a useful technique to modify the CNF surfaces for manufacturing of CNF composites especially when surface roughening of CNFs plays an important role in enhancing interfacial interaction with a polymer matrix.

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