

LARGE-AREA ROLL-TO-ROLL ATMOSPHERIC PLASMA TREATMENT OF NANOCELLULOSE TRANSPARENT PAPER

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Abstract

Cellulose, as the most abundant polymer in the world, and recently nanocellulose, have emerged as sustainable, biodegradable and recyclable substrates for flexible and printed electronics in applications that require rapid roll-to-roll manufacturing. However, the wetting and printability of any material surface are linked to its surface energy. These may be modified by cleaning and activation of the surface, i.e. removal, formation or alteration of the adventitious or functional chemical groups on it. Recently, novel surface treatment techniques compatible with roll-to-roll manufacturing have attracted considerable attention on the part of researchers. In this contribution, we present atmospheric-pressure plasma generated by diffuse coplanar surface barrier discharge (DCSBD) for the surface treatment of nanocellulose transparent paper. The effect of ambient-air, low-temperature plasma on the surface of nanocellulose was investigated. Water contact angle measurements revealed increased hydrophilicity of the surface after short plasma treatment. X-ray photoelectron spectroscopy was utilized for chemical analysis of the surface of the nanocellulose. Plasma treatment led to a decrease in carbon concentration and a corresponding increase in oxygen concentration. Analysis of carbon peaks in the spectra revealed decreased C-C bonds and the formation of oxygen polar groups. The formation of polar groups was directly related to the increased hydrophilicity. Scanning electron microscopy was used to observe the morphological effects of plasma treatment on the nanocellulose surface. No damage to the nanocellulose fibres was observed after plasma treatment, which confirms that low-temperature plasma is suitable for large-area roll-to-roll treatment of nanocellulose.

Keywords: Nanocellulose, plasma treatment, surface activation, roll-to-roll, printability

1. INTRODUCTION

Compatibility with rapid roll-to-roll manufacturing, along with its biodegradability and worldwide resource-abundance has made nanocellulose paper an attractive option as a substrate in flexible and printed electronics. Compared to naturally-occurring cellulose, which consists of cellulose fibres 20-50 μm in diameter, the microfibrils that make up nanocellulose paper have diameters that lie in a measurement range of only tens of nanometres. This allows nanocellulose paper to match the desirable properties of plastic substrates, such as low surface roughness and thermal stability, while adding recyclability and enhanced flexibility [1,2].

Solution-based printing is an ideal deposition technique for roll-to-roll manufacturing [3]; its throughput is high and the price is low. Among other options, nanocellulose has been actively studied as a substrate and a range of electronic devices utilizing such “paper” have been demonstrated, including flexible organic field-effect transistors (OFETs) [4], foldable antennas [5], and organic light-emitting diodes (OLEDs) [6].

The successful printing of different materials requires a range of properties on the part of the substrate surface. Plasma treatment of the surface influences the surface energy of the material, which is linked to its printability [6,7]. Depending on the working gas, widely differing degrees of surface wettability can be achieved. The hydrophilicity of the surface may be increased by treatment in oxygen plasma, while hydrophobicity may

be achieved by treatment in the plasma generated in gases containing halogens, H₂ or methane [9-11]. Moreover, even a “pristine” nanocellulose surface may contain contaminations; plasma treatment is capable of removing these, thus tailoring surface energy to practical requirements.

Surface activation refers to the formation, alteration or removal of chemical groups on the surface of the material by plasma. The increased hydrophilicity of the surface is linked to oxidation and formation of oxygen polar groups on the surface [12]. However, changes in surface morphology may also influence wettability. This effect is often undesirable as it may damage the surface and affect the mechanical properties and overall performance of the material.

In this contribution we present an ambient-air atmospheric-pressure plasma treatment of nanocellulose paper compatible with roll-to-roll processing. The diffuse coplanar surface barrier discharge (DCSBD) (see **Figure 1**) utilized herein provides high power density and a low working temperature, both compatible with nanocellulose paper. The macroscopically diffuse nature of the process provides a homogeneous surface treatment. Further, it does not lead to undesired pin-holing or other damage to the sample treated [7].



Figure 1 Diffuse coplanar surface barrier discharge (DCSBD) with curved configuration of electrodes

2. EXPERIMENTAL PROCEDURE

The nanocellulose paper was kindly provided by Dr. Juho Antti Sirviö of the Fibre and Particle Engineering Research Unit at the University of Oulu, Finland. The preparation process is thoroughly described in the works of *Sethi et. al.* and *Li et. al.* [13,15].

The plasma surface treatment was performed by means of atmospheric-pressure ambient-air plasma generated by diffuse coplanar surface dielectric barrier discharge (RPS400 for roll-to-roll, Roplasm s.r.o., Czech Republic) with a curved-coplanar configuration of electrodes (**Figure 1**). The plasma source has the capacity to deliver a power density 100 W/cm³. Plasma treatment times varied from 1 s to 16 s.

The water-contact angle (WCA) measurement was carried by means of the See System (Advex Instruments, Czech Republic) with a 1- μ l water droplet deposited on the surface using a micropipette. The image of the droplet was taken approximately 10 s after deposition.

The chemical analysis and the stoichiometry of the surface were determined using X-ray photoelectron spectroscopy (XPS), with an ESCALAB 250Xi (ThermoFisher Scientific) instrument using the Al K α spectral line. All samples were measured at one spot, with a take-off angle of 90° in 10⁻⁵ Pa vacuum at 20 °C. An electron flood-gun was used to compensate for charges on the sample surface.

The effects of plasma treatment on the morphology of the nanocellulose surface were studied with a Mira3 (Tescan, Czech Republic) scanning electron microscope (SEM). Prior to analysis, the samples were coated

with a 20-nm-thick layer of gold and palladium mixture with a concentration ratio of Au : Pd = 80 : 20. The images were captured at 50 kx magnification, 5 kV accelerating voltage and at a working distance of 5 mm.

3. RESULTS AND DISCUSSION

WCA measurements were taken from untreated and plasma-treated samples. The results appear in **Figure 2** and **Table 1**. The reference sample exhibited a WCA of 72°. After plasma treatment of just 1 s, WCA dropped sharply to just 19°. Longer plasma treatment times did not lead to any further decrease in WCA. This result suggests a very rapid and effective surface modification of the nanocellulose paper by plasma, achieving considerably enhanced wettability of the surface after very short plasma treatment.

XPS was utilized for stoichiometric analysis of the reference and plasma-treated samples. Atomic percentages obtained from this analysis are summarized in **Table 1**. The untreated sample displayed concentrations of carbon and oxygen of 65.9 at. % and 34.1 at. %, respectively. Following 1 s of plasma treatment, the concentration of carbon dropped to 58.4 at. %, with oxygen concentration increasing to 41.6 at. %. Again, longer treatment times had only a slight effect on further stoichiometric changes.

The ratio of carbon to oxygen disclosed in the samples is plotted in **Figure 2**, together with the WCA results. A clear correlation between C/O ratio and WCA can be observed. The decreasing WCA can therefore be related to the decreasing C/O ratio. This may be explained by the oxidation effect of the plasma treatment producing new, oxygen-rich functional groups on the surface [14].

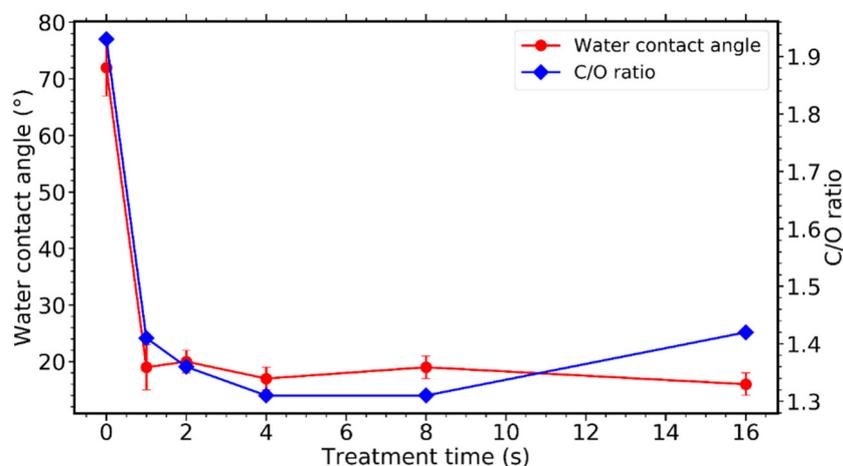


Figure 2 Water contact angle on nanocellulose paper and carbon-to-oxygen ratio obtained from XPS as functions of plasma treatment time

Table 1 XPS results of water contact angle measurements and concentrations of elements for a range of plasma treatment times

Treatment time (s)	WCA (°)	Carbon (at. %)	Oxygen (at. %)	C/O ratio
0	72 ± 5	65.9	34.1	1.93
1	19 ± 4	58.4	41.6	1.40
2	20 ± 2	57.6	42.4	1.36
4	17 ± 2	56.7	43.3	1.31
8	19 ± 2	56.7	43.3	1.31
16	16 ± 2	58.7	41.3	1.42

Figure 3 shows a high-resolution XPS peak of C1s obtained for the reference sample and the plasma-treated samples. The C1s peak of nanocellulose consists of chemical shifts that may be classified into four categories: unoxidized carbon (C-C); carbon with one oxygen bond (C-O-/C-OH); carbon with two oxygen bonds (O-C-O/C=O); and carbon with three oxygen bonds (O=C-O) [16]. The spectra were referenced to the C-C peak at 284.8 eV. Qualitative analysis of the C1s peak shows a pronounced decrease in the intensity of the C-C peak after very brief plasma treatment, just 1 s. This can be attributed to the breaking and oxidation of the unoxidized carbon bonds and to some extent to the removal of surface contamination arising out of plasma treatment [9].

SEM images of untreated and some plasma-treated samples appear in **Figure 4**. No particular morphological change is visible on the plasma-treated samples. The short plasma treatment at low temperature did not do any damage to the nanocellulose paper surface. Thus, the increased hydrophilicity arising out of the treatment can be attributed solely to changes in the chemical composition of the surface.

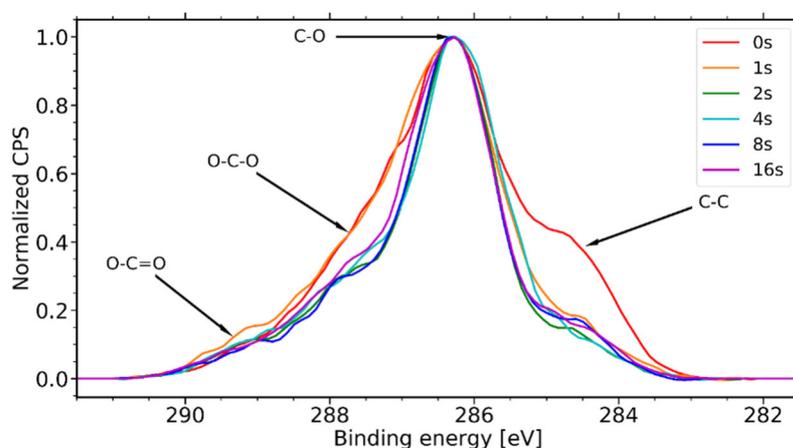


Figure 3 High resolution XPS peak C1s of untreated and plasma-treated nanocellulose paper with increasing treatment times.

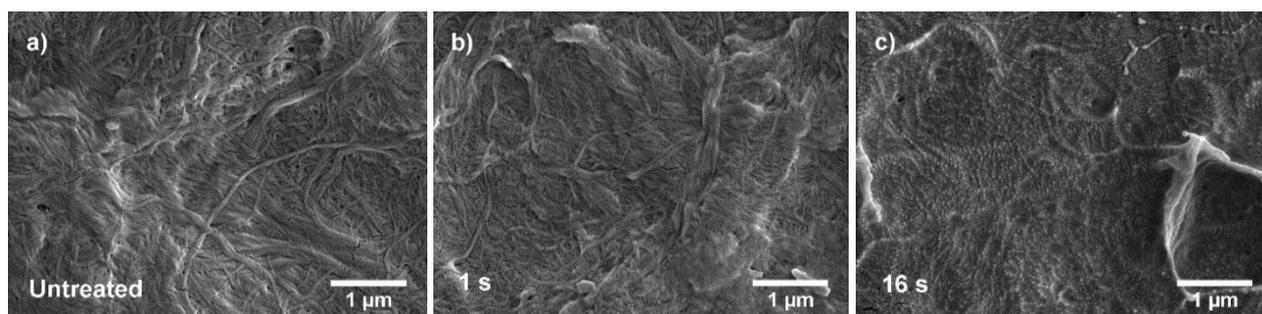


Figure 4 SEM images of nanocellulose a) untreated and plasma-treated for b) 1 s and c) 16 s

4. CONCLUSION

This contribution presents a study of the effects of atmospheric-pressure, ambient-air plasma generated by DCSBD for the surface treatment of nanocellulose paper. Hydrophilicity of the paper was successfully enhanced with very short treatment times (1 s). The increased wettability of the nanocellulose surface was linked to a decreased carbon/oxygen ratio. This arose out of plasma-induced oxidation of unoxidized C-C bonds on the surface and partly from removal of surface contamination. SEM images of untreated and plasma-treated nanocellulose surface showed no significant change in the morphology of the surface. It may be concluded, therefore, that the plasma treatment left the surface undamaged and any morphological changes had no effect the hydrophilization of the nanocellulose paper.

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