

1 Proceedings

2 Plasma-induced fibrillation and surface functionalization of 3 cellulose microfibrils †

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8 **Abstract:** The classical production of microfibrillar cellulose involves intensive mechanical pro-
9 cessing and discontinuous chemical treatment in solvent-based media in order to introduce addi-
10 tional chemical surface modification. By selecting appropriate conditions of a pulsed plasma reactor,
11 a solvent-free and low-energy input process can be applied with introduction of microcrystalline
12 cellulose (MCC) and maleic anhydride (MA) powders. The plasma processing results in the pro-
13 gressive fibrillation of the cellulose powder into its elementary fibril structure and in-situ modifica-
14 tion of the produced fibrils with more hydrophobic groups that provide good stability against re-
15 agglomeration of the fibrils. The selection of a critical ratio MA/MCC at 200 % (wt./wt.) allows to
16 separate the single cellulose microfibrils with changeable morphologies depending on the plasma
17 treatment time. Moreover, the density of the hydrophobic surface groups can be changed through
18 selection of different plasma duty cycle times, while the influence of plasma power and pulse fre-
19 quency is inferior. The variations in treatment time can be followed along the plasma reactor, as the
20 microfibrils gain smaller diameter and become somewhat longer with increasing time. This can be
21 related to the activation of the hierarchical cellulose structure and progressive diffusion of the MA
22 within the cellulose structure causing progressive weakening of the hydroxyl bonding. In parallel,
23 the creation of more reactive species with time allows to create active surface sites that allow for
24 interaction between the different fibrils into more complex morphologies. The in-situ surface mod-
25 ification has been demonstrated by XPS and FTIR analysis, indicating the successful esterification
26 between the MA and hydroxyl groups at the cellulose surface. In particular, the crystallinity of the
27 cellulose has been augmented after plasma modification. Furthermore, AFM evaluation of the fibrils
28 show surface structures with irregular surface roughness patterns that contribute to better interac-
29 tion of the microfibrils after incorporation in an eventual polymer matrix. In conclusion, the combi-
30 nation of physical and chemical processing of cellulose microfibrils provides a more sustainable
31 approach for fabrication of advanced nanotechnological materials.

32 **Keywords:** cellulose; plasma; microfibrils; surface modification

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2 been increasingly used as a green technology to enhance the sustainability of lignocellulosic materials [1].

3 The plasma modification of cellulose was studied under inert conditions in order to
4 verify the changes in surface conditions. In particular, surface ablation and changes in
5 surface morphology were observed in combination with morphological changes and
6 small reduction in fiber width [2]. The exposure to oxygen plasma induces localized de-
7 composition with formation of highly functionalized molecules. The bulk of the fibers was
8 selectively changed, where the crystalline zones remained unaffected through the plasma
9 treatment with consequent variations in physical and chemical properties [3]. Ultimately,
10 the depolymerization of cellulose in a non-thermal atmospheric plasma was achieved for
11 the conversion into glucose units [4]. The active species created from a plasma with reac-
12 tive gasses, e.g. when exposed the oxygen and sulfur hexafluoride, allows to create pat-
13 terned nanostructures on the cellulose fiber surfaces with both changes in surface chem-
14 istry and topography that are needed to change the hydrophilic properties of cellulose
15 into hydrophobic properties [5]. As a result, the plasma (pre-)treatment in combination
16 with gaseous reactants like oxygen, ethylene or silane allows to adapt the surface adhesive
17 properties when used as filler in composite materials and/or change the interaction with
18 bacterial environment [6]. The hydrophobic modification of more complex cellulose struc-
19 tures can be done using CCl_4 as plasma, acting solely on the surface without modifying
20 the bulk structure [7]. Alternatively, the surface modification of cellulose through chemi-
21 cal grafting with maleic anhydride is commonly used as a compatibilization step when
22 mixing cellulose into more hydrophobic matrix materials, but it is usually conducted by
23 wet-end chemical processing [8].

24 The microfibrillated cellulose (MFC) is a form of nanocellulose that is converted into
25 elementary fibrils, which is usually done through an intensive mechanical processing in-
26 volving high internal shear stresses and energy requirement [9]. The post-step function-
27 alization of cellulose nanomaterials can then be implemented by plasma modification [10].
28 This has been frequently implemented for cellulose nanocrystalline materials [11,12]. The
29 submerged liquid plasma processing was recently used for the fibrillation of cellulose in
30 combination with ultrasonic treatments in inert argon or reactive oxygen/nitrogen envi-
31 ronment to improve the dispersibility in water mixtures [13]. In contrast, the present work
32 starts from dried powders of cellulose and reactive maleic anhydride monomers intro-
33 duced in a pulsed plasma process, which allows for the simultaneous fibrillation of the
34 cellulose structure and stabilization by chemical grafting of maleic anhydride.

36 2. Experimental details

37 The microcrystalline cellulose (MCC) was introduced together with maleic anhy-
38 dride (MA) as powdery monomers. The precursors were inserted into a sealed glass tube
39 that was degassed several times and were later connected to the inlet of the plasma reac-
40 tor. A ratio of the monomers was selected according to their weight ratio $\text{MA/MCC} = 200$
41 % (wt./wt.) in order to get sufficient overload of the polymer relatively to the fibrous ma-
42 terial.

43 A cylindrical-shape glass container was used as a vacuum chamber that was con-
44 nected to a monomer gas inlet and pump, and surrounded by a copper coil driven by a
45 RG generator. In a pulsation mode, the power is switched on and off in micro-second
46 intervals and their ratio becomes important to calculate to effective power. The ratio has
47 mainly effect on the retention time of the functional groups in the plasma. In general, the
48 higher t_{off} time increase deposition thickness, while higher t_{on} times lead to significant
49 monomer fragmentation and loss of functional groups. The plasma conditions were se-
50 lected for the creation of the MCC and in-situ surface modification with MA according to
51 a pulsed plasma processing. Therefore, the maximum power of 20 W and fixed pulse fre-
52 quency 820 Hz were applied. The output of the pulsed plasma process is characterized by
53 selection of the cycling times, including the plasma-on time (i.e., cycling time for creation

of active species) $t_{on} = 25 \mu s$ and the plasma-off-time (i.e., cycling time for reaction and recombination) $t_{off} = 1200 \mu s$.

A characterization of the cellulose materials after plasma processing was done by optical microscopy (LOM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), atomic force microscopy (AFM) and X-ray photon spectroscopy (XPS).

3. Test results

The morphology of pulsed-plasma processed MCC is illustrated in Figure 1, including optimized plasma processing conditions that allow for the in-situ fibrillation of the cellulose structure. The processing of pure MCC resulted in the formation of particles (Figure 1a), resembling the sizes and morphologies of the original powder. It is evident that the plasma processing has no influence on the particle properties and surface modification is not possible, solely some charges may be introduced at the surface. However, agglomeration of several particles has not been observed. In case of a ratio MA/MCC = 200 w/w (Figure 1b), an impressive morphology develops where the single particles fibrillate into several separated elementary cellulose fibrils. This morphology was only observed at a critical weight ratio, where the presence of MA is favorable for the stabilization and dispersion of the single fibrils. The fibrillation process obviously proceeds depending

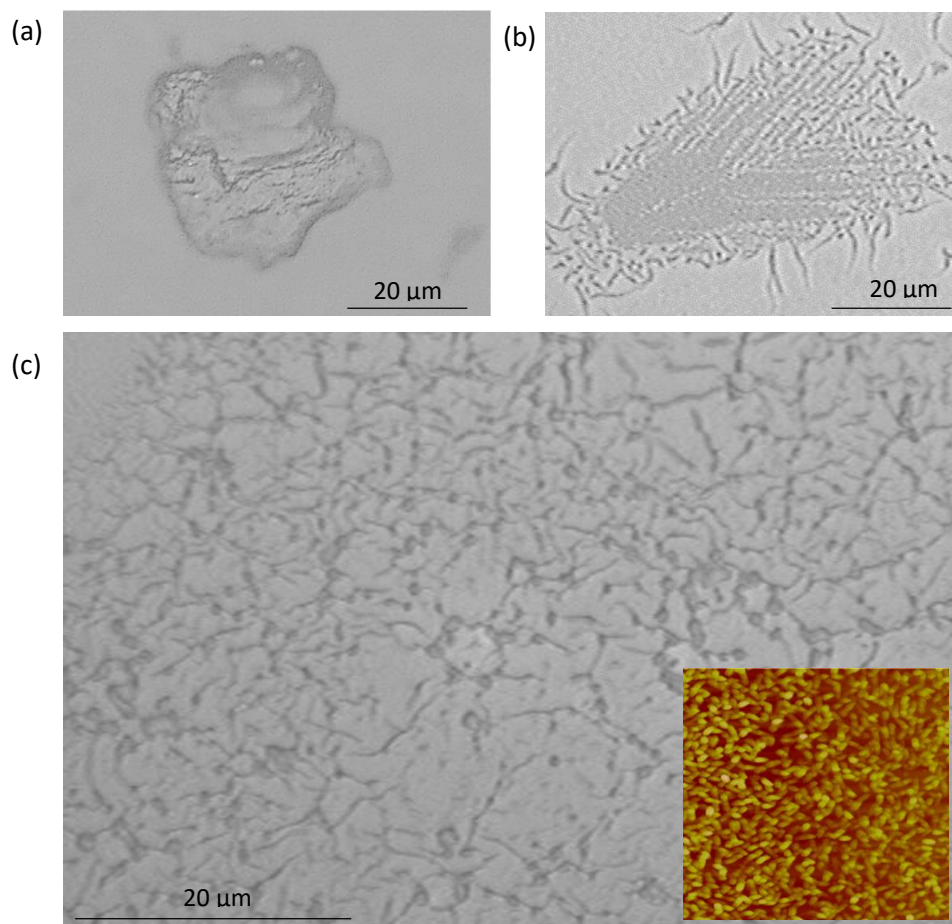


Figure 1. Optical microscopy of (a) original MCC, (b) starting of the fibrillation of the cellulose particles after plasma processing under optimized conditions with MA/MCC = 200 % (wt./wt.) (processing time $t = 10$ min), (c) formation of and MFC/MA network of surface-modified fibrillated cellulose with AFM inset ($10 \times 10 \mu m^2$), under optimized conditions with MA/MCC = 200 % (wt./wt.) (processing time $t = 30$ min).

on the processing time, where the hierarchical cellulose structure starts to open up after a processing time of 10 min, while the single fibrils get more loose and form a more complete fibrillar network structure after longer processing time (Figure 1c). Likely, the presence of MA allows for the diffusion in gaseous phase within the cellulose structure (more specific the amorphous zones) and the interaction of activated species in the plasma phase allows for simultaneous surface modification and formation of a dense MFC network.

The variations in chemical structure of the cellulose are confirmed by ATR-FTIR spectra of the processed fibers (Figure 2). The carbonyl region is characterized by a shift in the C=O band of closed-ring maleic anhydride (1800 cm^{-1}) for the original MA, towards an esterified C=O band (1750 cm^{-1}) for the plasma-processed MFC/MA. This confirms the chemical surface modification of the cellulose surface, with an esterification reaction localized near the hydroxyl groups of the cellulose. The structural variations in cellulose are observed near the C-O-C / C-OH band region (1060 cm^{-1}), which suggests variations in crystallinity of the processed MFC. The sharper bands and narrowing of the band are typical for structural variations that include reorientation or confinement of the backbone in cellulose structure into more ordered phase. The fibrillation of the cellulose during plasma processing may likely result in removal of more disordered cellulose zones and creation of fibrils with an enhanced structural organization.

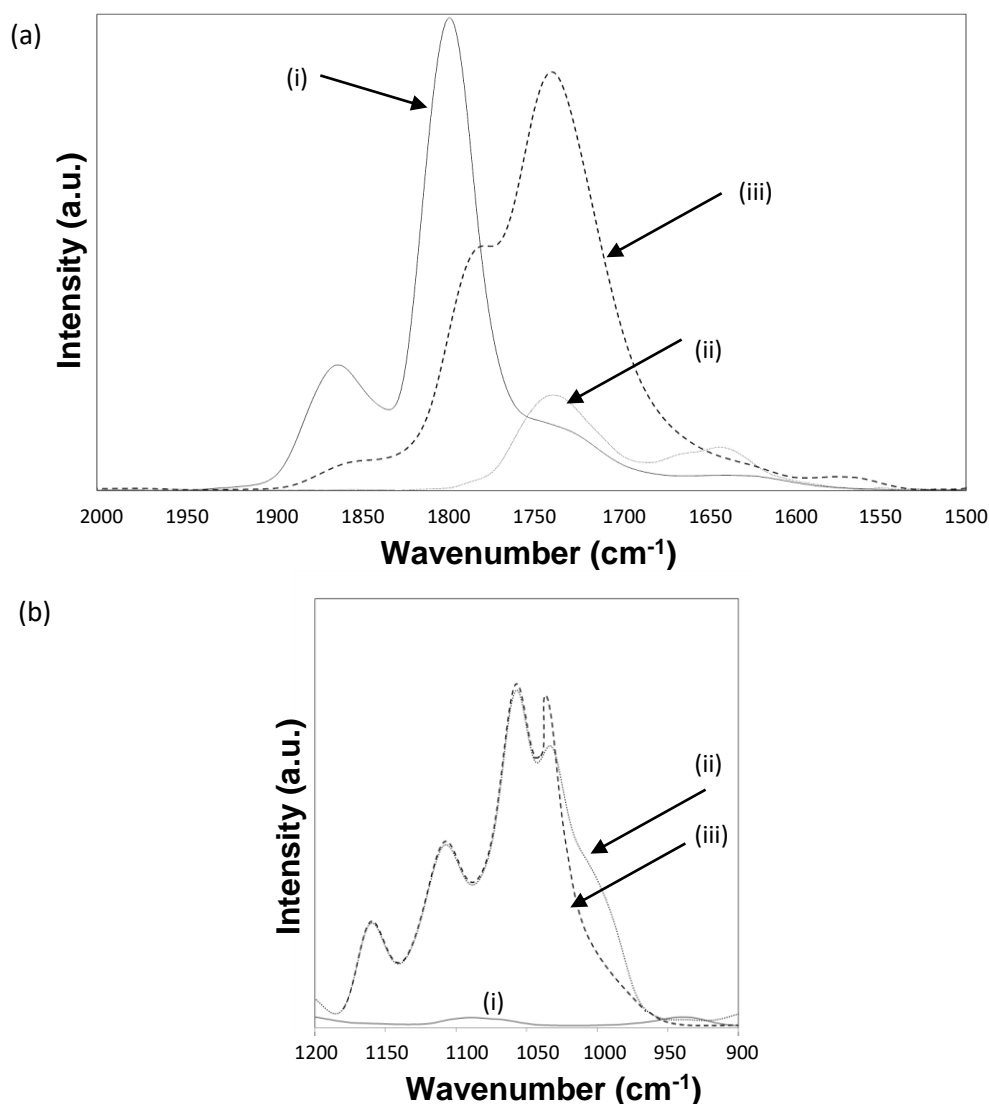


Figure 2. Detail of the ATR-FTIR spectra in wavenumber regions 2000 – 1500 cm^{-1} , or (b) 1200 – 900 cm^{-1} , for (i) MA , (ii) MCC and (iii) modified MFC/MA after plasma processing.

The XPS results of the high-resolution C1s peak are compared in Figure 3 for the plasma-polymerized MA and MFC/MA. The typical peaks for MA plasma polymers include **1** hydrocarbons (285.0 eV, C-C, CH_x); **2** carbon in alpha position of anhydride/carboxylic acids, esters (285.6 eV, C-C=O); **3** carbon single bonds to oxygen (286.6 eV, C-O); **4** carbon double bonds to oxygen (287.9 eV, C=O); **5** anhydride groups, carboxylic acid, ester groups (289.5 eV, O=C-O-C=O, O-C=O). The calculation of atomic concentrations based on the surface area beneath the respective peaks, indicates significant differences for pure MA compared to MFC/MA. The peak **1** is representative of hydrocarbons formed through monomer fragmentation and is lower for the MFC/MA compared to pure MA, as the likelihood for crosslinking in the pure plasma polymer between single MA moieties reduces in presence of MFC. Alternatively, the peak **2** indicative for esterification reaction is significantly enhanced for MFC/MA due to favorable chemical surface modification of the cellulose with MA. Finally, the peak **5** representing closed-ring anhydride groups is slightly lower for the MFC/MA than for pure MA as a confirmation for the ring-opening reaction and esterification. However, the intensity ratio of peak ratio 3 (C-OH) relatively to peak 4 (O-C-O) is lower for plasma-modified MFC than for pure cellulose (which should be around 5 : 1), confirming that an important amount of the cellulose C-OH disappears through ring-opening and esterification with MA.

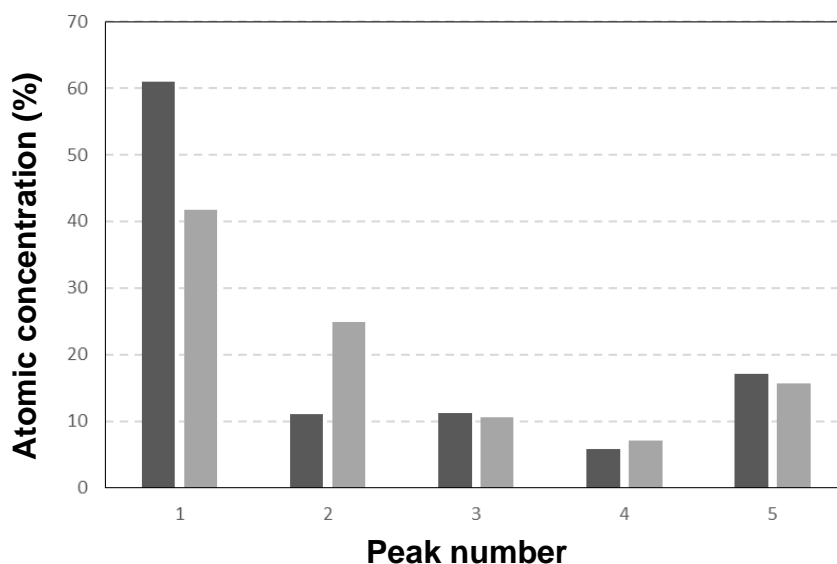


Figure 3. Atomic concentration of different functionalities present in the high-resolution C1s peak obtained by XPS analysis for MA (black bars), and MFC/MA (grey bars). Peak numbers **1**, **2**, **3**, **4**, **5** are explained in the text.

4. Conclusions

The simultaneous fibrillation of cellulose and surface modification with maleic anhydride (MA) has been successfully demonstrated during a pulsed plasma polymerization process of MA, after selecting the optimized plasma processing conditions and a critical ratio of cellulose / MA monomer. The fibrillation is gradually visualized by an opening of the fine fibrillar structure of cellulose and stabilization of the dispersion state of the fibrils. The chemical surface modification of the cellulose fibrils through esterification reaction with MA has been demonstrated by additional chemical analysis. The characterization of surface modification agrees between XPS and FTIR spectra, while the latter also suggests variations in phase ordering of the cellulose molecules after processing. As such, the feasibility for plasma processing as a sustainable approach for fabrication of microfibrillated cellulose has been demonstrated.

1 References

- 2 1. Vanneste, J.; Ennaert, T.; Vanhulsel, A.; Sels, B. Unconventional pretreatment of lignocellulose with low-temperature plasma.
3 *Chem. Sus. Chem.* **2017**, *10*, 14-31.
- 4 2. Kolarova, K.; Vosmanska, V.; Rimpelova, S.; Svorcik, V. Effect of plasma treatment on cellulose fiber. *Cellulose* **2013**, *20*, 953-961.
- 5 3. Calvimontes, A.; Mauersberger, P.; Nitschke, M.; Dutschk, V.; Simon, F. Effects of oxygen plasma on cellulose surface. *Cellulose*
6 **2011**, *18*, 803-809.
- 7 4. Benoit, M.; Rodriguez, A.; Zhang, Q.; Fourré, E.; De Oliveira Viger, K.; Raribouet, J.M.; Jerome, F. Depolymerization of cellulose
8 assisted by a nonthermal atmospheric plasma. *Angew. Chem. Int. Ed.* **2011**, *50*, 8964-8967.
- 9 5. De Camargo, J.S.; de Menezes, A.J.; da Cruz, N.C.; Rangel, E.C.; Delgado-Silva, A. Morphological and chemical effects of plasma
10 treatment with oxygen (O₂) and sulfur hexafluoride (SF₆) on cellulose surface. *Mat. Res.* **2017**, *20*, 842-850.
- 11 6. Mauger, O.; Westphal, S.; Klopzing, S.; Kruger-Genge, A.; Muller, W.; Storsberg, J.; Bohrish, J. Plasma activation as a powerful
12 tool for selective modification of cellulose fibers towards biomedical applications. *Plasma* **2020**, *3*, 196-203.
- 13 7. Shi, J.; Lu, L.; Guo, W.; Sun, Y.; Cao, Y. An environment-friendly thermal insulation material from cellulose and plasma modi-
14 fication. *J. Appl. Polym. Sci.* **2013**, *130*, 3652-3658.
- 15 8. Cichosz, S.; Masak, A.; Rylski, A. Cellulose modification for improved compatibility with the polymer matrix: mechanical char-
16 acterization of the composite material. *Materials* **2020**, *13*, 5519.
- 17 9. Osong, S.H.; Norgren, S.; Engstrand, P. Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and
18 applications relating to papermaking: a review. *Cellulose* **2016**, *23*, 93-123.
- 19 10. Chanda, S.; Bajwa, D.S. A review of current physical techniques for dispersion of cellulose nanomaterials in polymer matrices.
20 *Rev. Adv. Mater. Sci.* **2021**, *60*, 325-341.
- 21 11. Alanis, A.; Valdes, J.H.; Guadalupe, N.V.M.; Lopez, R.; Mendoza, R.; Mathew, A.P.; de Leon, R.D.; Valencia, L. Plasma surface-
22 modification of cellulose nanocrystals: a green alternative towards mechanical reinforcement of ABS. *RSC Adv.* **2019**, *9*, 17417-
23 17424.
- 24 12. Matouk, Z.; Rincon, R.; Torriss, B.; Mirzaei, A.; Margot, J.; Chaker, M. Functionalization of cellulose nanocrystals powder by
25 non-thermal atmospheric-pressure plasmas, *Cellulose* **2021**, *28*, 6239-6252.
- 26 13. Vizireanu, S.; Panaitescu, D.M.; Nicolae, C.A.; Frone, A.N.; Chiulan, I.; Ionita, M.D.; Satuly, V.; Carpen, L.G.; Petrescu, S.; Birjega,
27 R.; Dinescu, G. Cellulose defibrillation and functionalization by plasma in liquid treatment. *Sci. Reports* **2018**, *8*, 15473.
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