proceedings

Proceedings

Plasma-induced fibrillation and surface functionalization of cellulose microfibrils †

Pieter Samyn [1,*]

[1] Analytical and Circular Chemistry, Hasselt University, Agoralaan Gebouw D, B-3590 Diepenbeek, Belgium
* Correspondence: pieter.samyn@outlook.be

† Presented at 2nd International Electronic Conference on Applied Sciences

Abstract: The classical production of microfibrillar cellulose involves intensive mechanical processing and discontinuous chemical treatment in solvent-based media in order to introduce additional chemical surface modification. By selecting appropriate conditions of a pulsed plasma reactor, a solvent-free and low-energy input process can be applied with introduction of microcrystalline cellulose (MCC) and maleic anhydride (MA) powders. The plasma processing results in the progressive fibrillation of the cellulose powder into its elementary fibril structure and in-situ modification of the produced fibrils with more hydrophobic groups that provide good stability against reagglomeration of the fibrils. The selection of a critical ratio MA/MCC at 200 % (wt./wt.) allows to separate the single cellulose microfibrils with changeable morphologies depending on the plasma treatment time. Moreover, the density of the hydrophobic surface groups can be changed through selection of different plasma duty cycle times, while the influence of plasma power and pulse frequency is inferior. The variations in treatment time can be followed along the plasma reactor, as the microfibrils gain smaller diameter and become somewhat longer with increasing time. This can be related to the activation of the hierarchical cellulose structure and progressive diffusion of the MA within the cellulose structure causing progressive weakening of the hydroxyl bonding. In parallel, the creation of more reactive species with time allows to create active surface sites that allow for interaction between the different fibrils into more complex morphologies. The in-situ surface modification has been demonstrated by XPS and FTIR analysis, indicating the successful esterification between the MA and hydroxyl groups at the cellulose surface. In particular, the crystallinity of the cellulose has been augmented after plasma modification. Furthermore, AFM evaluation of the fibrils show surface structures with irregular surface roughness patterns that contribute to better interaction of the microfibrils after incorporation in an eventual polymer matrix. In conclusion, the combination of physical and chemical processing of cellulose microfibrils provides a more sustainable approach for fabrication of advanced nanotechnological materials.

Keywords: cellulose; plasma; microfibrils; surface modification

Citation: Samyn, P. Plasma-induced fibrillation and surface functionalization of cellulose microfibrils . *Proceedings* **2021**, *68*, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

The plasma processing of fibers offers an ecologically-friendly method for surface activation and functionalization of the fibers. The plasma-induced surface modification and interface engineering benefits from solvent-free handling of the reactive species and in-situ formation of the coupled materials through a combination of physical processes. The plasma phase is a complex state where particles of a gaseous phase are converted through radical reactions into a variety of active species, i.e. excited atoms and molecules, ionized moieties, electros, free radicals and ionic complexes. As an advantage, the laboratory set-ups for plasma modification can be smoothly scaled-up towards (semi-)industrial units for fast and flexible processing of materials. Therefore, plasma treatment has been increasingly used as a green technology to enhance the sustainability of lignocellulosic materials [1].

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

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

2. Experimental details

The microcrystalline cellulose (MCC) was introduced together with maleic anhydride (MA) as powdery monomers. The precursors were inserted into a sealed glass tube that was degassed several times and were later connected to the inlet of the plasma reactor. A ratio of the monomers was selected according to their weight ratio MA/MCC = 200 % (wt./wt.) in order to get sufficient overload of the polymer relatively to the fibrous material.

A cylindrical-shape glass container was used as a vacuum chamber that was connected to a monomer gas inlet and pump, and surrounded by a copper coil driven by a RG generator. In a pulsation mode, the power is switched on and off in micro-second intervals and their ratio becomes important to calculate to effective power. The ratio has mainly effect on the retention time of the functional groups in the plasma. In general, the higher t_{off} time increase deposition thickness, while higher t_{on} times lead to significant monomer fragmentation and loss of functional groups. The plasma conditions were selected for the creation of the MCC and in-situ surface modification with MA according to a pulsed plasma processing. Therefore, the maximum power of 20 W and fixed pulse frequency 820 Hz were applied. The output of the pulsed plasma process is characterized by selection of the cycling times, including the plasma-on time (i.e., cycling time for creation of active species) t_{on} = 25 µs and the plasma-off-time (i.e., cycling time for reaction and recombination) t_{off} = 1200 µs.

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

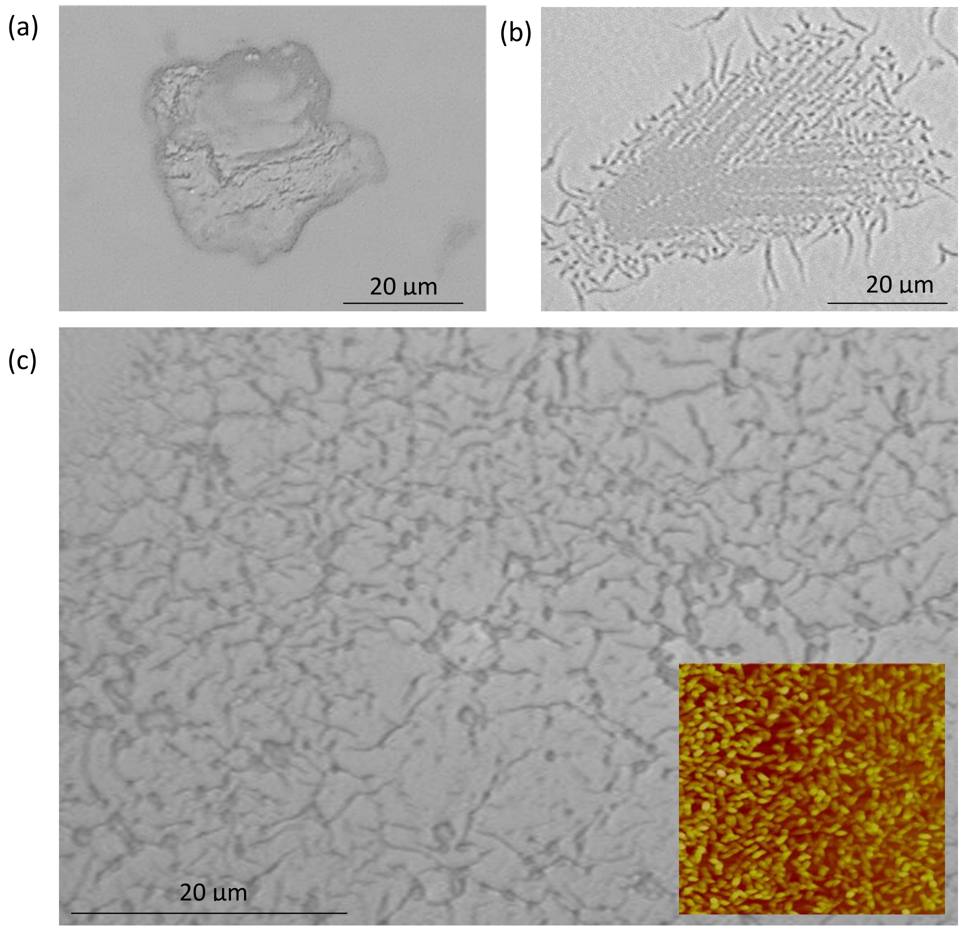

Figure 1. Optical microscopy of (a) original MCC, (b) starting of the fibrillation of the cellulose particles after plasma processing under optimized conditions with MA/MCC = 200 % (wt./wt.) (processing time t = 10 min), (c) formation of and MFC/MA network of surface-modified fibrillated cellulose with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

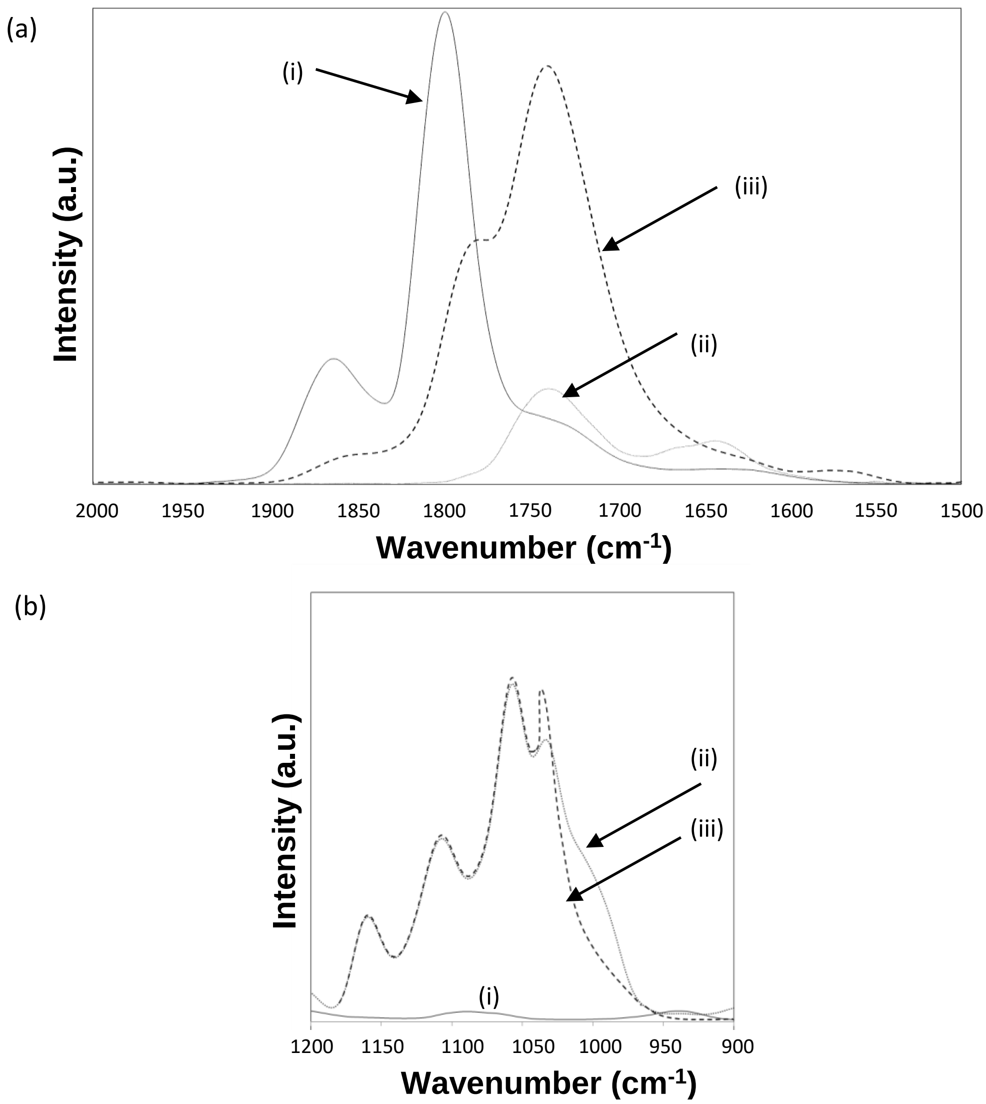

Figure 2. Detail of the ATR-FTIR spectra in wavenumber regions 2000 – 1500 cm^{-1}, or (b) 1200 – 900 cm^{-1}, for (i) MA , (ii) MCC and (iii) modified MFC/MA after plasma processing.

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** hydrocarabons (285.0 eV, **C**-C, **C**H_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 likeliness 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.

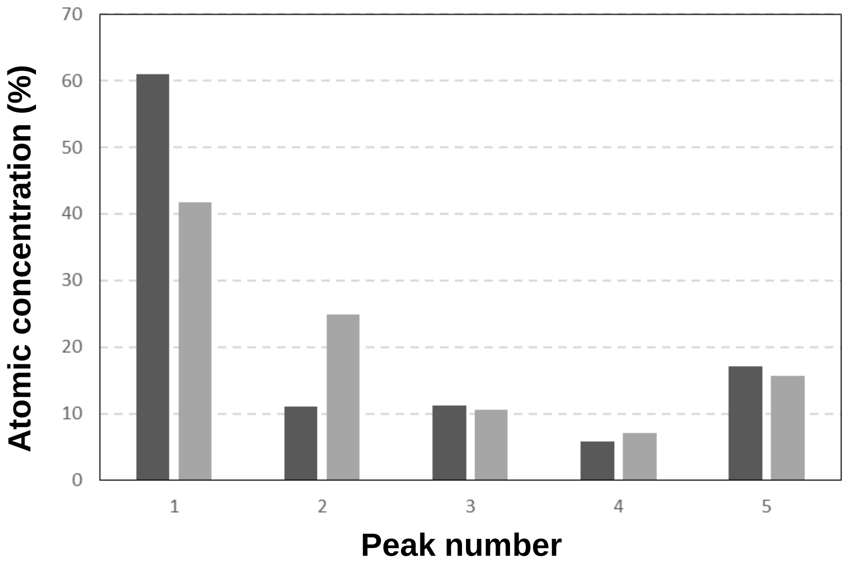

Figure 3. Atomic concentration of different functionalities present in the high-resolution C1s peak obtained by XPS analysis for MA (black bars), and MFC/MA (grey bars). Peak numbers **1**, **2**, **3**, **4**, **5** are explained in the text.

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.

References

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