

PLASMA MODIFICATION OF LIGNOCELLULOSIC TEXTILE MATERIALS

ANA KRAMAR^{1*}, BILJANA PEJIĆ¹, BRATISLAV OBRADOVIĆ²,
MILORAD KURAICA² and MIRJANA KOSTIĆ¹

¹*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
11000 Belgrade, Serbia*

E-mail akramar@tmf.bg.ac.rs, biljanap@tmf.bg.ac.rs, kostic@tmf.bg.ac.rs

²*Faculty of Physics, University of Belgrade, Studentski trg 12, 11000 Belgrade,
Serbia*

E-mail obrat@ff.bg.ac.rs, kuki@ff.bg.ac.rs

Abstract. Plasma modification of textiles has a great potential to replace conventional wet chemical methods and becomes one of the leading processes in textile finishing. Plasma devices opposite to the wet treatments have many advantages, i.e. small energy and no chemical consumption, reduced duration of the treatment, and ease of implementation into existing facilities. In this work, atmospheric pressure dielectric barrier discharge (DBD) was used for modification of hemp (lignocellulosic) fibers with different chemical composition. Raw hemp (containing cellulose, lignin and hemicelluloses), hemp fibers with low content of lignin and with low content of hemicelluloses were used as experimental material. Wettability of each type of fibers increased significantly due to the changes in fibers morphology analyzed by SEM. The highest wettability improvement (estimated by measurement of capillary rise) was recorded for samples with lower content of hemicelluloses, followed by raw hemp fibers. Having in mind that wettability of hemp is conventionally improved by chemical treatments, this work shows that plasma processing can be successfully used for lignocellulosic fibers modification.

1. INTRODUCTION

Lignocellulosic materials, such are hemp, flax and jute, represent very unique type of fibers. They have heterogenic structure, main constituent being cellulose, with significant amount (15-20 %) of noncellulosic components such are pectin, waxes, lignin and hemicelluloses (Lazić et al. 2018). Hemp fibers (lat. *Cannabis Sativa*) can have various applications, e.g. as textile material for clothing and technical textile production, as composite material reinforcement, as biosorbent for wastewater treatment and removal of heavy metal ions etc. (Wang et al., 2003). In order to be used as textile material, lignocellulosic fibers must be subjected to various chemical treatments to remove non cellulose components without cellulose damage (Wang et al., 2003). Removal of these components influences hydrophylicity of lignocelluloses fibers, by changing their sorption properties. Different conventional chemical treatments are being used to remove noncellulosic components. However, using plasma treatment instead chemical procedures is a

challenge with outstanding potential, due to the possibility to reduce environmental impact of chemical processing. The main advantage of plasma treatment of textiles is that it is a surface treatment while bulk of material is preserved. Furthermore, plasma treatment is a dry method, does not require use of water or any chemicals except gas (Shishoo, 2007). However, there are only few reports about plasma treatment of lignocellulose fibers. In the paper by Ibrahim et al. (2010) air DBD was used to improve wettability, increase functional groups and surface roughness of flax fibers. Li et al. (2014) used the DBD in helium after pretreatment of ramie fibers in ethanol and plasma treatment to improve interfacial adhesion between ramie fibers and poly(butylene succinate) PBS, a thermoplastic polymer. Ventura et al. (2016) studied the effect of plasma treatment on the flax nonwoven intended to be used as a composite reinforcement and they studied several types of plasma, both atmospheric pressure plasma (APP) and low pressure plasma. Hydrophilicity of flax material was significantly increased when APP in air was used.

In this work, atmospheric pressure DBD in air was used for modification of hemp fibers. Hemp fibers with different contents of hemicelluloses and lignin were used in order to determine the sensitivity of hemp constituents to the plasma treatment and to compare effects of chemical processing and plasma on wettability of hemp fibers.

2. EXPERIMENTAL MATERIALS AND METHODS

1.1. EXPERIMENTAL MATERIAL

Raw hemp fibers from Backi Brestovac (Serbia) were used as experimental material. To obtain different precursors for DBD treatments, hemp fibers were modified with 17.5 % sodium hydroxide for 5 and 45 min (to remove hemicelluloses) and 0.7 % sodium chlorite for 5 and 60 min (to remove lignin), as described in literature by Pejic et al. (2020).

1.2. PLASMA TREATMENT

Hemp fibers were treated with DBD plasma device described by Pejic et al. (2020) following regime of discharge 80 W, 10 kV, 300 Hz, 60 Jcm^{-2} , and treatment time of 2 min.

1.3. MORPHOLOGY STUDIES (SEM)

Investigation of surface morphology was carried out with scanning electron microscopy (SEM), using a JEOL 840A instrument, on samples previously coated with gold using a JFC 1100 ion sputter.

1.4. WETTABILITY MEASUREMENT AND SORPTION PROPERTIES

Wettability of samples was characterized by capillary rise method according to the procedure described by Pejic et al. (2020). Water retention power (WRP) was measured by standardized centrifuge method according to ASTM D 2402 – 01 (2001) in triplicate for each sample.

3. RESULTS AND DISCUSSION

In this work DBD in air was used for hemp fibers modification. The starting materials were fibers with various quantities of hemicelluloses and lignin (Fig 1), in order to study the effect of plasma on different components (cellulose, hemicellulose and lignin).

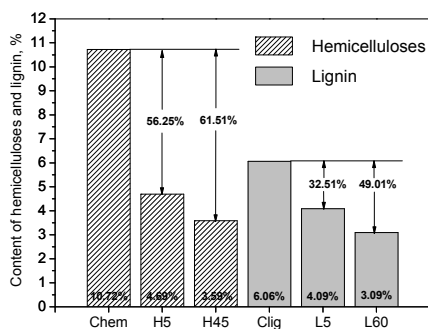


Figure 1: Composition of hemp fibers precursors used for DBD treatments

After plasma treatment, wettability, i.e. equilibrium height during capillary rise, was the highest for hemp fibers with lower content of hemicelluloses (H5 and H45) (Fig 2a) while wettability of raw hemp fibers (C) and fibers with lower content of lignin (L5 and L60) increased about 5 and 2 times, respectively. The significant change of surface morphology contributed to these results of improved sorption (Fig 2b). Compared to the raw hemp fibers and hemp with lower content of hemicelluloses (C and H5), plasma treated samples (C300 and H5/300) have more pronounced surface roughness which promotes better wettability. This confirms the surface targeted treatment of used DBD.

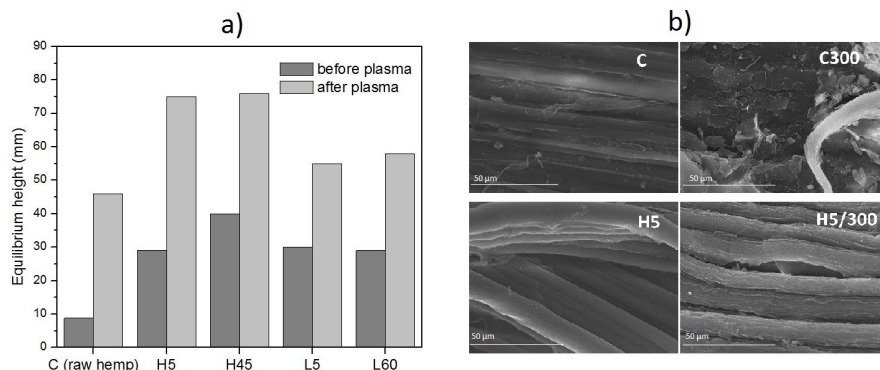


Figure 2: The effect of DBD in air on a) wettability and b) morphology of raw hemp (C) and hemp fibers with lower content of hemicelluloses (H5 and H45) and with lower content of lignin (L5 and L60) (Pejic et al. 2020)

Water retention power is sorption property related to the entire sample not just the surface of material. WRP represents the total water holding capacity of all

voids and pores in the fiber structure (Lazić et al. 2018). Therefore, we have examined the influence of plasma treatment on WRP, and found that it is almost unchanged by plasma treatment (Fig 3). It can be concluded that even though plasma influences capillarity and morphology of samples, plasma effect is limited to the surface, while bulk of material and properties related to the bulk such is WRP underwent almost no changes after plasma treatment. Initial increase of WRP of precursor hemp fibers L5 and L60 (with lower content of lignin) remained the same after plasma treatment and exhibited the highest WRP of all samples.

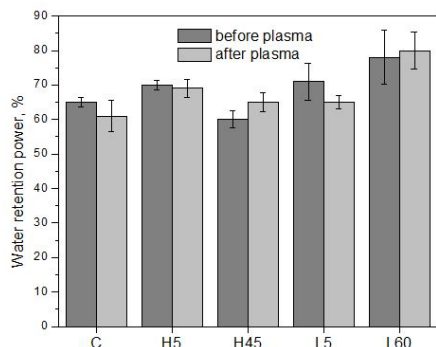


Figure 3: Water retention power (WRP) of different hemp samples before and after plasma treatment

CONCLUSION

In this work, DBD treatment was applied on hemp fibers with different content of hemicelluloses and lignin. Plasma treatment of raw hemp fibers led to a significant improvement of wettability (5 times) estimated through capillary rise. The maximum equilibrium height was obtained by DBD treatment of hemp fibers with lower content of hemicelluloses (H5 and H45). Improved wettability is mainly the consequence of change in fibers morphology while the bulk of material is preserved which was corroborated by no changes in water retention power, i.e. property related to the bulk of material. Overall, this investigation showed that plasma has a potential to substitute the chemical treatments for some applications of hemp, which require improved wettability or increased surface roughness.

References

- Ibrahim, N. A., Hashem, M. M., Eid, M. A., Refai, R., El-Hossamy, M., Eid, B. M.: 2010, *The Journal of The Textile Institute*, **101**, 1035.
- Lazić, B. D., Pejić, B. M., Kramar, A. D., Vukčević, M. M, Mihajlovski, K. R., Rusmirović, J. D., Kostić, M. M.: 2018, *Cellulose*, **25**, 697.
- Li, Y., Zhang, J., Cheng, P., Shi, J., Yao, L., Qui, Y.: 2014, *Industrial Crops and Products*, **61**, 16.
- Pejic, B. M., Kramar, A. D., Obradovic, B. M., Zekic, A., Kuraica, M. M., Kostic, M. M.: 2020, *Carbohydrate Polymers*, **236**, 116000.
- Shishoo, R.: 2007, *Plasma Technologies for Textiles*, Woodhead Publishing Limited, Cambridge.
- Ventura, H., Claramunt, J., Navarro, A., Rodriguez-Perez, M. A., Ardany, M.: 2016, *Materials*, **9**, 93.
- Wang, H., Postle, R., Kessler, R., Kessler, W.: 2003, *Textile Research Journal*, **73**, 664.