EFFECTS OF CELLULOSE NANOFIBRILS ON THE STRUCTURE AND PROPERTIES OF POLY(VINYL ALCOHOL) ELECTROSPUN NANOFIBERS

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ABSTRACT

Nanofibres of poly(vinyl alcohol) (PVA) reinforced with cellulose nanofibrils (CNFs) and/or crosslinked with maleic anhydride (MA) were produced by electrospinning technique to compare the additivation effects of the polymeric matrix. The results suggested that the PVA mass fraction equal to 14% and CNFs volumetric fraction of 3% are the best proportions for renewable base fibres production. CNFs addition allows to improve nanofibre thermal properties, which result in an eco-friendlier, biocompatible and biodegradable final product. In this study, different solutions required different operation conditions for a good membranes production and fibers with diameters between (70 to 140) nm were obtained.

INTRODUCTION

Cellulose nanofibrils (CNFs), have been considered as a promising reinforcing agent, because they show high crystallinity, stiffness, mechanical strength, high thermal stability, low weight, renewability, biodegradability, biocompatibility and non-toxicity (Nechyporchuk, 2016). Electrospinning is a simple and versatile technique used for the production of ultrathin and continuous nanofibres, which consists in applying a strong electric field to the polymeric solution (Haider, 2018). PVA can be reinforced with CNFs, since both have a great amount of hydroxyl groups, ensuring a satisfactory interfacial interaction by hydrogen bonding (Jiang, 2018). The objectives of this work were to produce composite membranes from PVA and CNFs by electrospinning technique and compare the individual and combined additivation effects of the PVA with CNFs and a chemical crosslinking agent studying solution parameters (viscosity and electrical conductivity) and process variables (applied voltage, feed rate, polymer concentration, tip-to-collector distance and collector type).

RESULTS AND CONCLUSIONS

Solutions with different concentrations of PVA (8 %, 11 %, 12 %, 14 % and 20 %) were prepared and tested. Studies from the solution with 20 % were not pursued, because this formulation promoted undesired drops deposition. Also, different CNFs volumes were tested (1 %, 3 %, 5 %, 10 %, 20 %) and it was verified that for solutions with CNF ≤ 3 % the solution dripping, during testing, did not occur. Regarding the PVA/MA formulation, better results were obtained from the solution with PVA=14% and molar ratio of MA equal to 20:1. Therefore, the samples was prepared using the following formulations: solution with PVA=14%; PVA=14%+CNF=3%; PVA=14%+MA20:1; PVA=14%+MA20:1+CNF=3%.

The equipment parameters effect in the fibres production was evaluated at different applied voltages (18 or 24 kV), tip collector distance (14.5 or 11.5 cm), feed rate (0.2 or 0.3 mL h^{-1}) and collector type (plate or rotating drum). In Fig. 1 and Table 1 the Scanning Electron Microscopy (SEM) and the experimental conditions of the best results are shown, respectively.

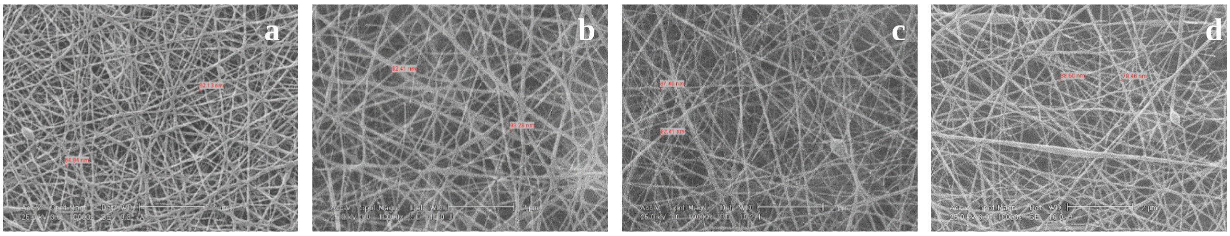

Fig. 1 SEM image of the best results for electrospun PVA (a), PVA+CNF (b), PVA+MA (c) and PVA+CNF+MA (d)

Table 1 Best results for the variation of equipment parameters for production of nanofibres

	Applied voltage (kV)	Tip-collector distance (cm)	Feed rate (mL h^{-1})	Collector type	Average fiber diameter (nm)
PVA	18	14.5	0.2	Plate	80-90
PVA+CNF	24	14.5	0.2	Drum	80-95
PVA+MA	24	14.5	0.2	Drum	80-90
PVA+MA+CNF	24	14.5	0.3	Plate	80-90

The results suggested that $x_{PVA} = 14$ % and $y_{CNF} = 3$ % are the best proportions for the production of renewable base fibres. For this formulation, the best spinning conditions were: applied voltage equal to 24 kV; feed rate equal to 0.2 mL h^{-1}; tip-to-collector distance equal to 14.5 cm; with cylinder rotating collector. FTIR results allowed confirming the presence and interaction of CNF and MA with the PVA matrix. The thermal properties of nanofibres analysed by TGA and DSC were improved when it was added the CNFs and/or the MA. However, it was verified that the CNFs effect seems to be better than the MA effect in the thermal stability of the mats until 320 °C. Moreover, cellulose becomes the composite nanofibres ecologically more sustainable, keeping important properties, such as biocompatibility and biodegradability, in the final product. So, in certain conditions and applications, it is possible and more advantageous to use a renewable raw material at a lower cost.

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REFERENCES

Nechyporchuk, O., Belgacem, M. N., & Bras, J. (2016). Production of cellulose nanofibrils: A review of recent advances. Industrial Crops and Products, 93, 2-25.

Haider, A., Haider, S., & Kang, I. K. (2018). A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology. Arabian Journal of Chemistry, 11(8), 1165-1188.

Jiang, S., Chen, Y., Duan, G., Mei, C., Greiner, A., & Agarwal, S. (2018). Electrospun nanofiber reinforced composites: a review. Polymer Chemistry, 9(20), 2685-2720.