Composites made of PVA and aramid nanofibers capable of simulating the properties of human cartilage tissue

A.S. Oliveira [1,2,3], R. Colaço [2], A.P. Serro [1,3], N.A. Kotov [4]

[1] CQE, IST, UL, Lisbon, Portugal; [2] idMEC, IST, UL, Lisbon, Portugal; [3] CiiEM, IUEM, Caparica, Portugal; [4] BI, UM, Ann Arbor, MI, US.

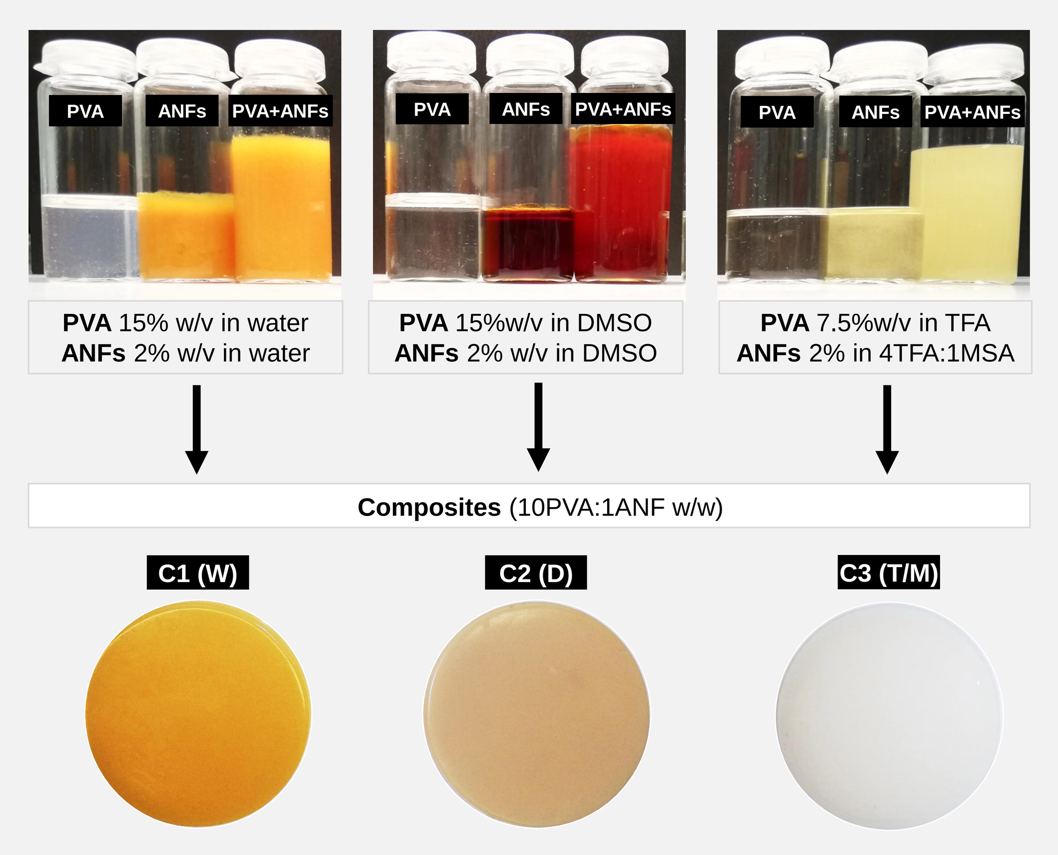
INTRODUCTION

Aramid (poly(p-phenylene terephthalamide)) fibers, commercially known as Kevlar, are a class of organic materials with outstanding properties, such as mechanical robustness and thermal stability [1]. These fibers have been widely used to reinforce other polymers, improving their stiffness and strength. Recently, it has been shown that a nanoscale version of Kevlar - aramid nanofibers (ANFs) synthesized from their macroscale fabrics and yarns - can effectively reinforce polyvinyl alcohol (PVA) for the replacement of cartilage tissues, due to their proven biocompatibility and exceptional mechanical properties [2].

OBJECTIVES

In this work, we prepare PVA+ANF composites under different conditions, to identify which production method can generate materials with superior mechanical and tribological performance, without compromising their water-retention ability, relevant in the mimicking of the natural tissues.

MATERIALS



METHODS

SEM

FEG-SEM (JSM−7001F, JEOL).

Samples dried by the tert-butyl alcohol freeze-drying method.

Materials coated with Au/Pd.

Swelling

Microscale (Discovery DV215CD, OHAUS Corporation).

Samples dried until reach the equilibrium.

$$\text{Swelling (\%)} = \frac{W_{water}}{W_{wet\ sample}} \times 100$$

Friction

Pin-on-disk tribometer (TRB³, Anton Paar). Reciprocal linear mode.

Counterbody: 316L stainless steel (Ø6 mm balls); Load: 5 and 20 N; Sliding velocity: 25 mm/s; Distance: 12 m; Stroke: 8 mm; Lubricant: PBS solution; Room temperature.

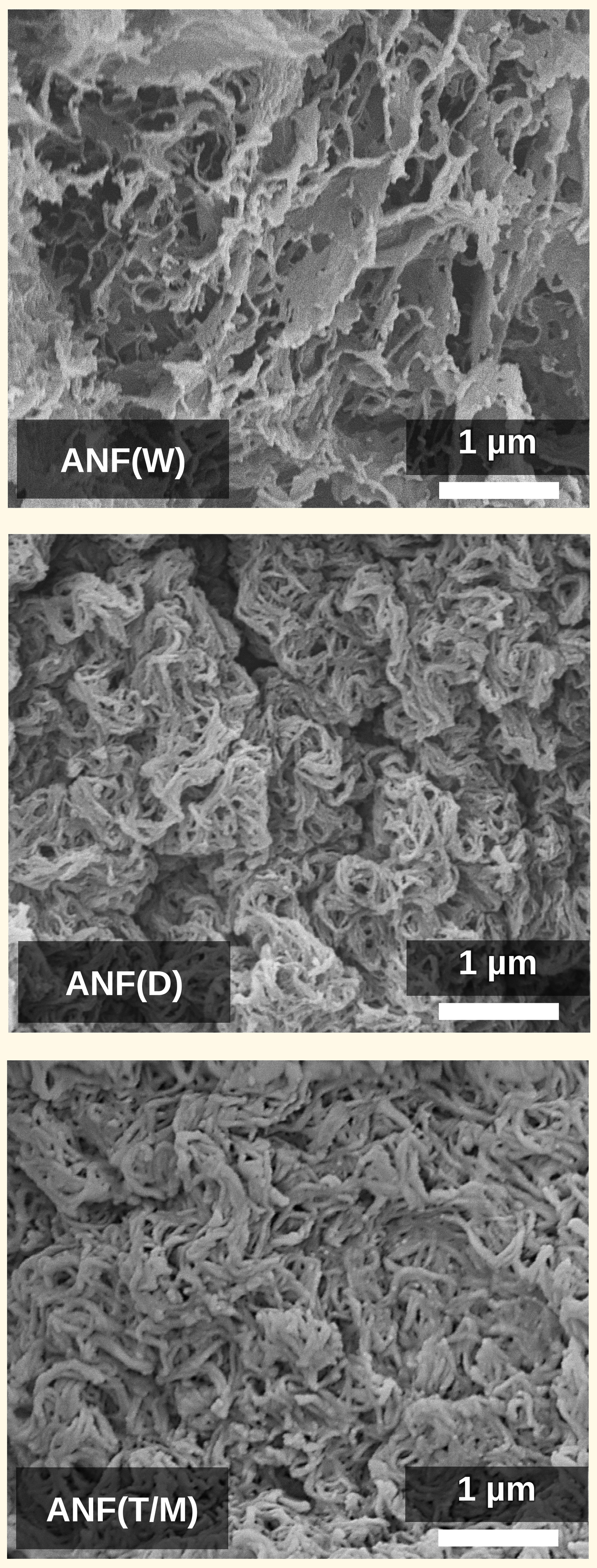
Compression / Tensile

Texturometer (TA.XT Express Texture Analyser, Stable Micro Systems). Uniaxial mode.

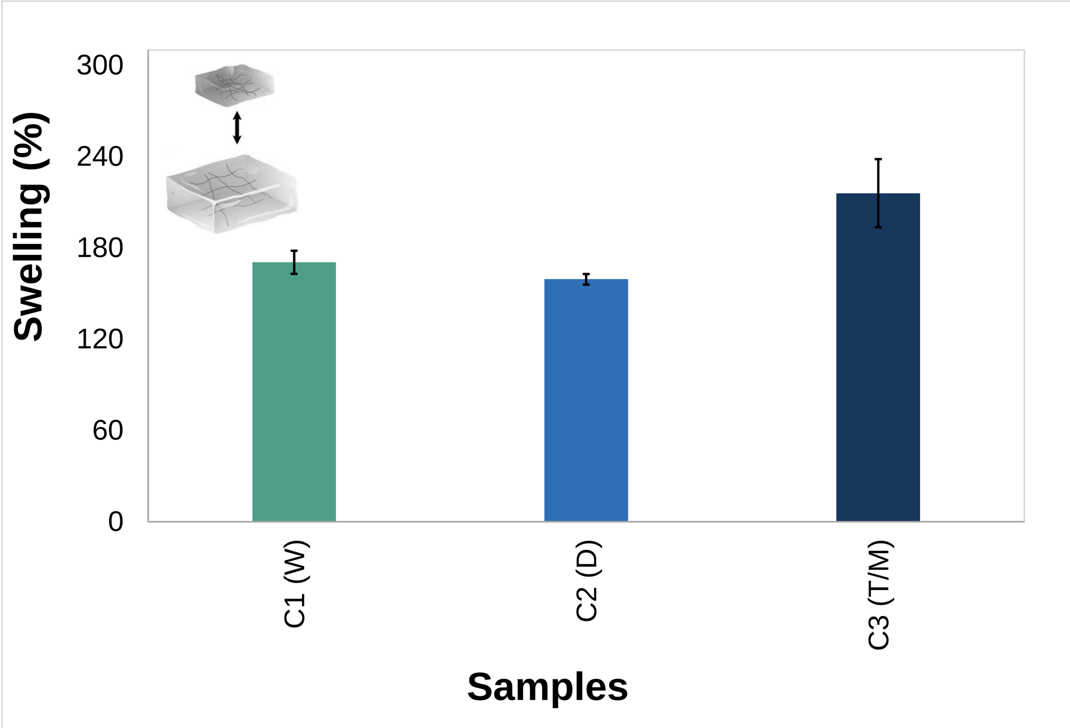
Compression: Performed at 37ºC, in unconfined mode. V = 0.1 mm/s. <u>Limit</u>: F = 50N.

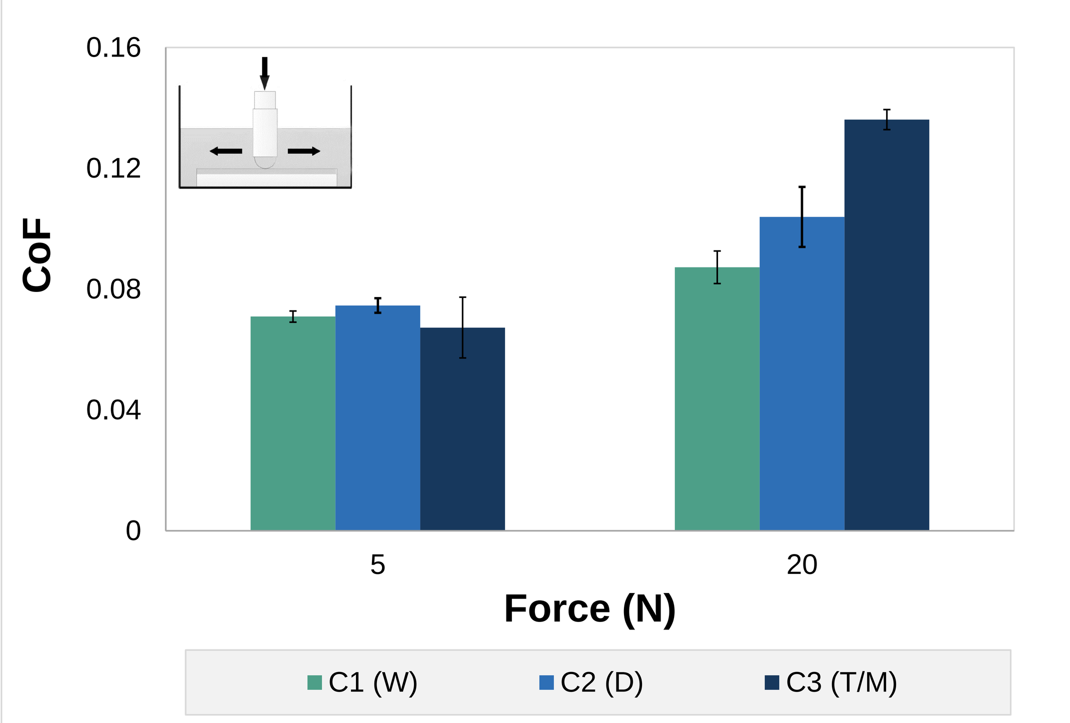
Tensile: Performed at room temperature. V = 0.5 mm/s. <u>Limit</u>: Until it break.

RESULTS AND DISCUSSION

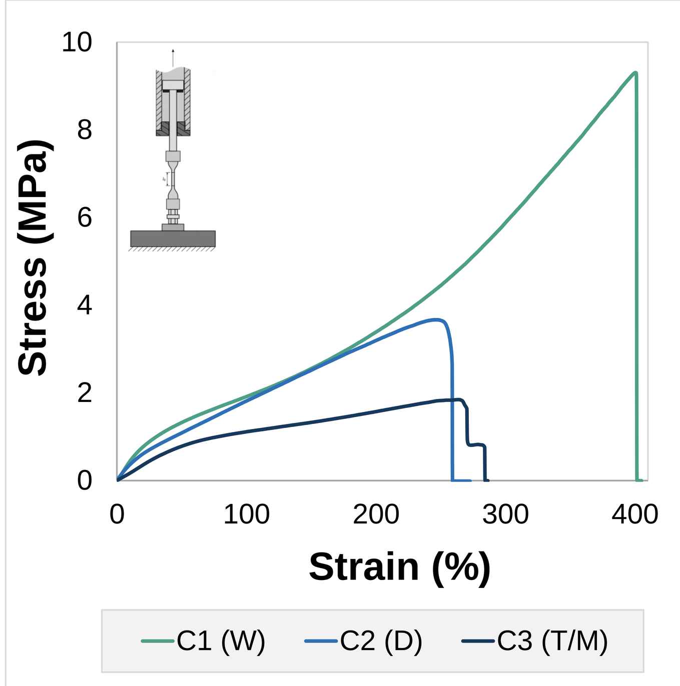


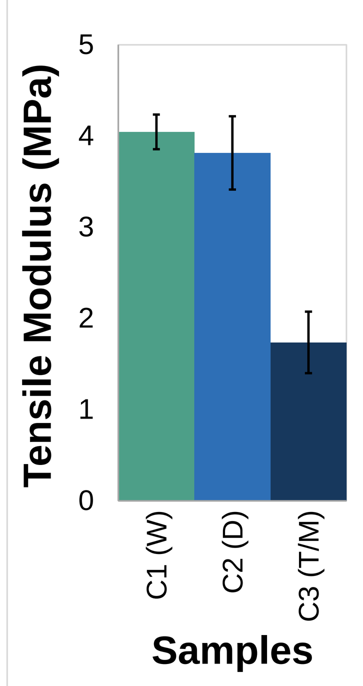
SEM micrographs of ANF samples prepared in water, DMSO or TFA/MSA are displayed in Figure 1. The images show the microscale morphology of ANFs, in which the nanofibers form a highly interconnected network.

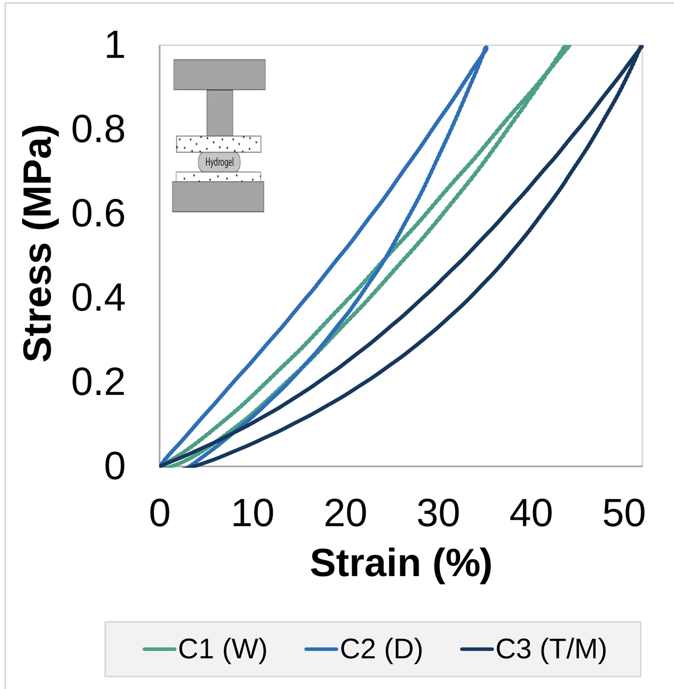


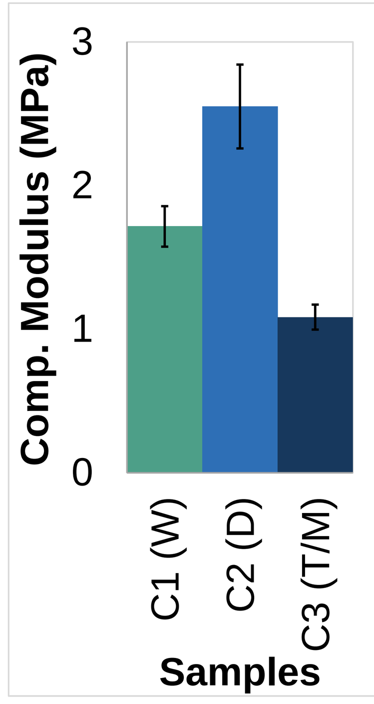


The swelling of hydrogels increased in the following order C2(D) < C1(W) < C3(T/M). Concerning tribological performance, the CoFs of all composites were low and similar (≈0.07) when 5 N of force was applied. For 20 N, C_W samples had the lowest CoF value (≈0.09). Concerning tribological performance, the CoFs of all composites were low and similar (≈0.07) when 5 N of force was applied. For 20 N, C_W samples had the lowest CoF value (≈0.09).









C1(W) samples exhibited a superior mechanical resistance under tensile stress compared to all others, showing higher values of ultimate strength (up to 4.8x) and failure strain (≈ 1.6x). In response to compression, C2(D) materials were the most rigid, presenting a modulus of ≈2.6 MPa and a maximum strain of ≈36%.

CONCLUSION

Our results indicated that the properties of PVA+ANF composites are dependent on the preparation method. ANF materials made from corresponding hydrogels, prepared in water (C1(W)) had an improved mechanical and tribological performance, without compromising their water-retention ability. The unique combination of properties should be attributed to the establishment of dense networks of hydrogen bonding interactions between the PVA and nanofibers.

REFERENCES

[1] García, JM, García, FC, Serna, F, de la Peña, JL, 'High-performance aromatic polyamides', *Prog. Polym. Sci.*, 35, 623–686 (2010): 10.1016/j.progpolymsci.2009.09.002.
[2] Xu, L, Zhao, X, Xu, C, Kotov, NA, 'Water-Rich Biomimetic Composites with Abiotic Self-Organizing Nanofiber Network', *Adv. Mater.*, 30, 1703343 (2018): 10.1002/adma.201703343.
[3] Lyu, J, Wang, X, Liu, L, Kim, Y, Tanyi, EK, Chi, H, Feng, W, Xu, L, Li, T, Noginov, MA, Uher, C, Hammig, MD, Kotov, NA, 'High Strength Conductive Composites with Plasmonic Nanoparticles Aligned on Aramid Nanofibers', *Adv. Funct. Mater.*, 26, 8435–8445 (2016):10.1002/adfm.201603230.
[4] Lv, L, Han, X, Zong, L., Li, M, You, J, Wu, X, Li, C, 'Biomimetic Hybridization of Kevlar into Silk Fibroin: Nanofibrous Strategy for Improved Mechanic Properties of Flexible Composites and Filtration Membranes', *ACS Nano.*, 11 8178–8184 (2017): 10.1021/acsnano.7b03119.
[5] Osatake, H, Inoué, T, 'A new drying method of biological specimens for scanning electron microscopy: The t-butyl alcohol freeze-drying method', *Arch. Histol. Cytol.*, 51, 53–59 (1988): 10.1679/aohc.51.53.

Acknowledgments

The authors gratefully acknowledge to Fundação para a Ciência e a Tecnologia for the financial support (grant numbers: PD/BD/128140/2016 [A.S. Oliveira, MIT - Portugal program], PTDC/CTM-CTM/29593/2017 [CartHeal], UIDB/00100/2020 [CQE], UIDB/50022/2020 [IDMEC/LAETA], and UIDB/04585/2020 [CiiEM]).

BIOMAT Research group
https://biomatlabgroup.wixsite.com/biomatresearchgroup/

E-mail: andreia.oliveira@tecnico.ulisboa.pt