Electrospinning of bioactive polycaprolactone-gelatin nanofibres with increased pore size for cartilage tissue engineering applications

Ângela Semitela[a], André F. Girão[a], Carla Fernandes[a], Gonçalo Ramalho[a], Igor Bdikin[a], António Completo[a]* and Paula A.A.P. Marques[a]*

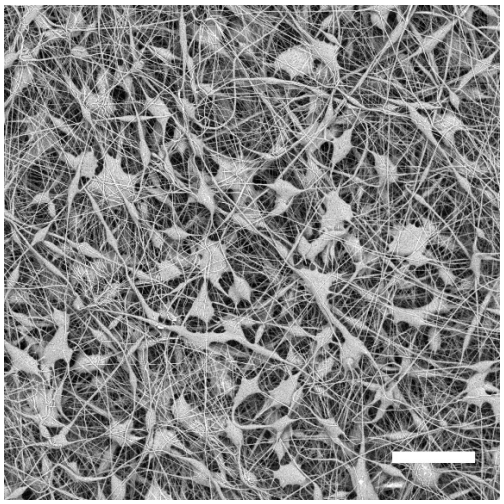
[a] TEMA, Department of Mechanical Engineering, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

* Corresponding author:

Paula A.A.P. Marques and António Completo
E-mail addresses: paulam@ua.pt and completo@ua.pt

Supplementary Material

It was not possible to obtain uniform and beadless fibres with 10% (w/v) PCL in only TFE, as depicted in the SEM image (Fig. S1 a). This phenomenon could be attributed to the high viscosity of the TFE (Fig. S1 b). In fact, there have been reports of incomplete drying of the polymer fibres when high viscosity solutions were used [4]. Since DMF has lower viscosity (Fig. S1 b), a substantial reduction of the viscosity of the resulting solution was expected, and it was probably the reason why beadless fibres were obtained using DMF as an additive. Besides the viscosity, the addition of DMF to the solvent system increased the solution dielectric constant (Fig. S1 b), allowing a higher amount of free and inducible charge in the PCL solution. Similar conclusions have been reported by researchers who also added DMF to methylene chloride [5] and dichloromethane [6] in order to obtain PCL fibres.



a)

b)

	2,2,2-trifluoethanol (TFE)	**n,n-dimethylformamide (DMF)**
Molecular weight	100.04	73.10
Density (g/cm^3)	1.39	0.99
Boiling point (ºC)	74[1]	153[2]
Viscosity (mPa·s)	1.78[1]	0.82[2]
Dielectric constant	8.55[3]	36.70[2]

Figure S1. SEM image of PCL fibrous scaffold using only TFE as solvent (a) and the TFE and DMF solvent properties (b). Scale bar: 50 μm.

PCL scaffolds did not display a significant mass loss over the 14-day period of incubation. On the contrary, a significant mass loss occurred on the PCL+GEL scaffolds within the first 24 hours of incubation in PBS, which can be attributed to GEL depletion.

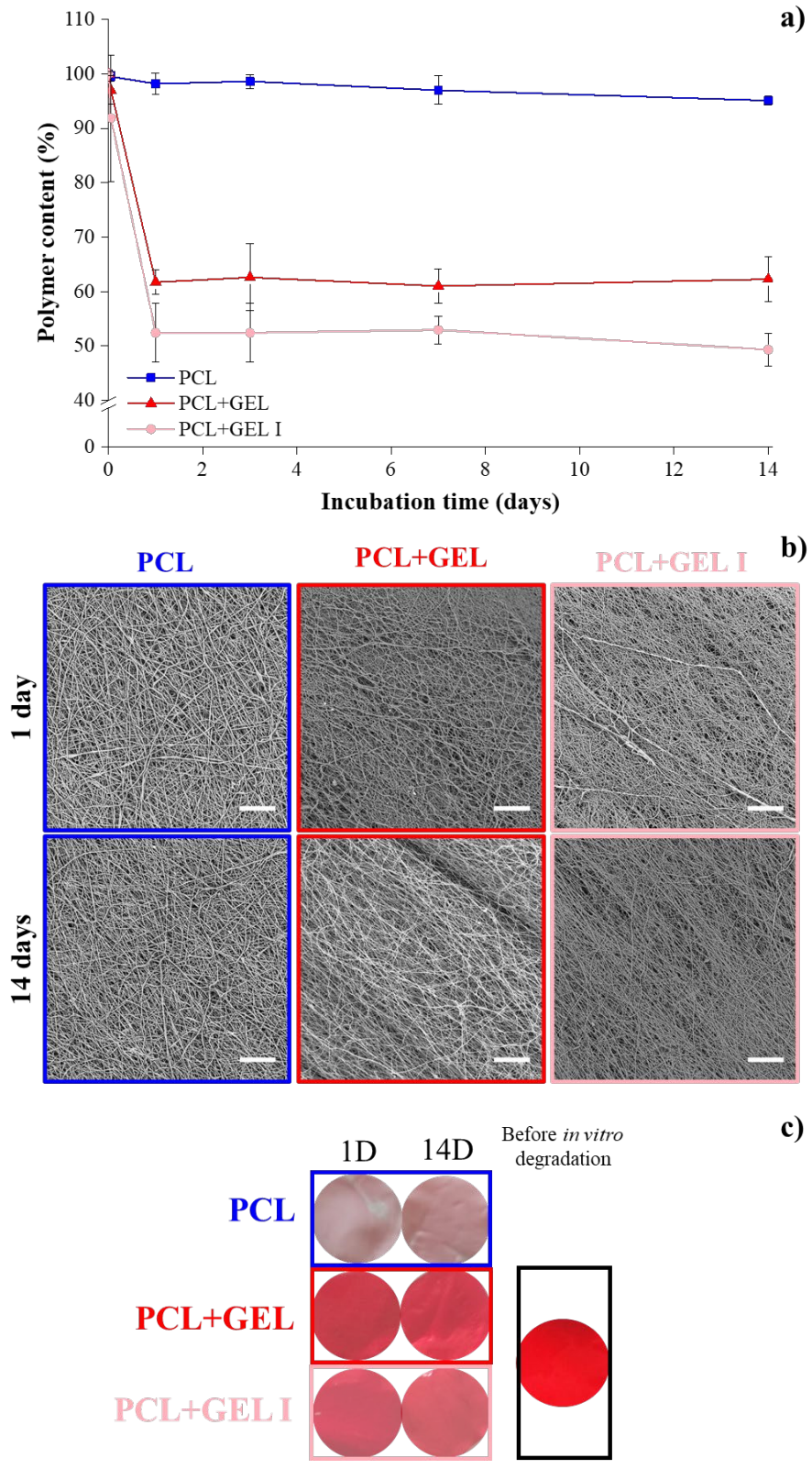


Figure S2. Polymer mass loss after biodegradation normalized to the polymer mass of PCL, PCL+GEL and PCL+GEL I (immersed only in PBS) (a), and the respective SEM images of the treated samples (b); Picrosirius red staining of PCL, PCL+GEL and PCL+GEL I scaffolds (c). Scale bar: 30 µm.

References

(1) Marcus, Y. Recommended Methods for the Purification of Solvents and Tests for Impurities: 1,2-Ethanediol and 2,2,2-Trifluoroethanol. *Pure Appl. Chem.* **1990**, *62* (1), 139–147. https://doi.org/10.1351/pac199062010139.

(2) Luo, C. J.; Stride, E.; Edirisinghe, M. Mapping the Influence of Solubility and Dielectric Constant on Electrospinning Polycaprolactone Solutions. *Macromolecules* **2012**, *45* (11), 4669–4680. https://doi.org/10.1021/ma300656u.

(3) Choktaweesap, N.; Arayanarakul, K.; Aht-ong, D.; Meechaisue, C.; Supaphol, P. Electrospun Gelatin Fibers: Effect of Solvent System on Morphology and Fiber Diameters. *Polym. J.* **2007**, *39* (6), 622–631. https://doi.org/10.1295/polymj.pj2006190.

(4) Pillay, V.; Dott, C.; Choonara, Y. E.; Tyagi, C.; Tomar, L.; Kumar, P.; Du Toit, L. C.; Ndesendo, V. M. K. A Review of the Effect of Processing Variables on the Fabrication of Electrospun Nanofibers for Drug Delivery Applications. *J. Nanomater.* **2013**, *2013* (789289), 22. https://doi.org/10.1155/2013/789289.

(5) Lee, K. H.; Kim, H. Y.; Khil, M. S.; Ra, Y. M.; Lee, D. R. Characterization of Nano-Structured Poly(ε-Caprolactone) Nonwoven Mats via Electrospinning. *Polymer (Guildf).* **2003**, *44* (4), 1287–1294. https://doi.org/10.1016/S0032-3861(02)00820-0.

(6) Du, L.; Xu, H.; Zhang, Y.; Zou, F. Electrospinning of Polycaprolatone Nanofibers with DMF Additive: The Effect of Solution Proprieties on Jet Perturbation and Fiber Morphologies. *Fibers Polym.* **2016**, *17* (5), 751–759. https://doi.org/10.1007/s12221-016-6045-3.