

DEVELOPMENT AND CHARACTERIZATION OF LIGNIN/POLYCAPROLACTONE NANOSTRUCTURES BY ELECTROSPINNING



J.F. Rubio-Valle, C. Valencia, M.C. Sánchez, J.E. Martín-Alfonso, José M. Franco

Pro²Tecs-Chemical Process and Product Technology Research Centre, Dept. Chemical Engineering and Materials Science, ETSI, Universidad de Huelva, Campus El Carmen 21071 Huelva (Spain)

Introduction

Electrospinning is one of the most important techniques in the manufacture of polymer nanofibers [1]. Despite this process was patented more than eighty years ago, until relatively recently, no special attention has been paid to this technology [2]. Its great interest is due to the extraordinary possibilities offered by the nanostructures designed that provide small size and high surface/volume ratio [3, 4]. Therefore, the objective of this work was to develop nanostructured membranes of Eucalyptus Kraft lignin (EKL), which was doped in small quantities with polycaprolactone (PCL), in order to improve their formation during the electrospinning process. For this, the properties of the solutions were evaluated through rheological, electrical conductivity, and surface tension tests. In addition, the morphological and functional characterization of the nanostructures obtained was carried out.

Experimental

Preparation EKL:PCL membranes



EKL and EKL:PCL solutions in DMF and chloroform were manufactured at 20 wt.% and the different EKL/PCL ratios can be seen in Table 1. Subsequently, the solutions were electrospun using the equipment of the trademark DOXA Microfluidics (Spain).

Rheological Properties



The viscosities of the systems were obtained in a controlled-strain rheometer (TA-Instruments, USA).

Surface Tension



The surface tension measurements were carried out using a force tensiometer (Biolint Science, China)

Electrical Conductivity



The electrical conductivity measurements of the different solutions were carried out with a Crison (Spain) meter

Morphological Properties



Morphological characterization of EKL/PCL nanostructures was carried out by means of scanning electron microscopy (SEM) in a JEOL, model JXA-8200 SuperProbe microscope operating at an acceleration voltage of 15 kV and different magnifications. Samples were previously gold-coated using a sputter coater HHV Scancoat Six SEM.

Results

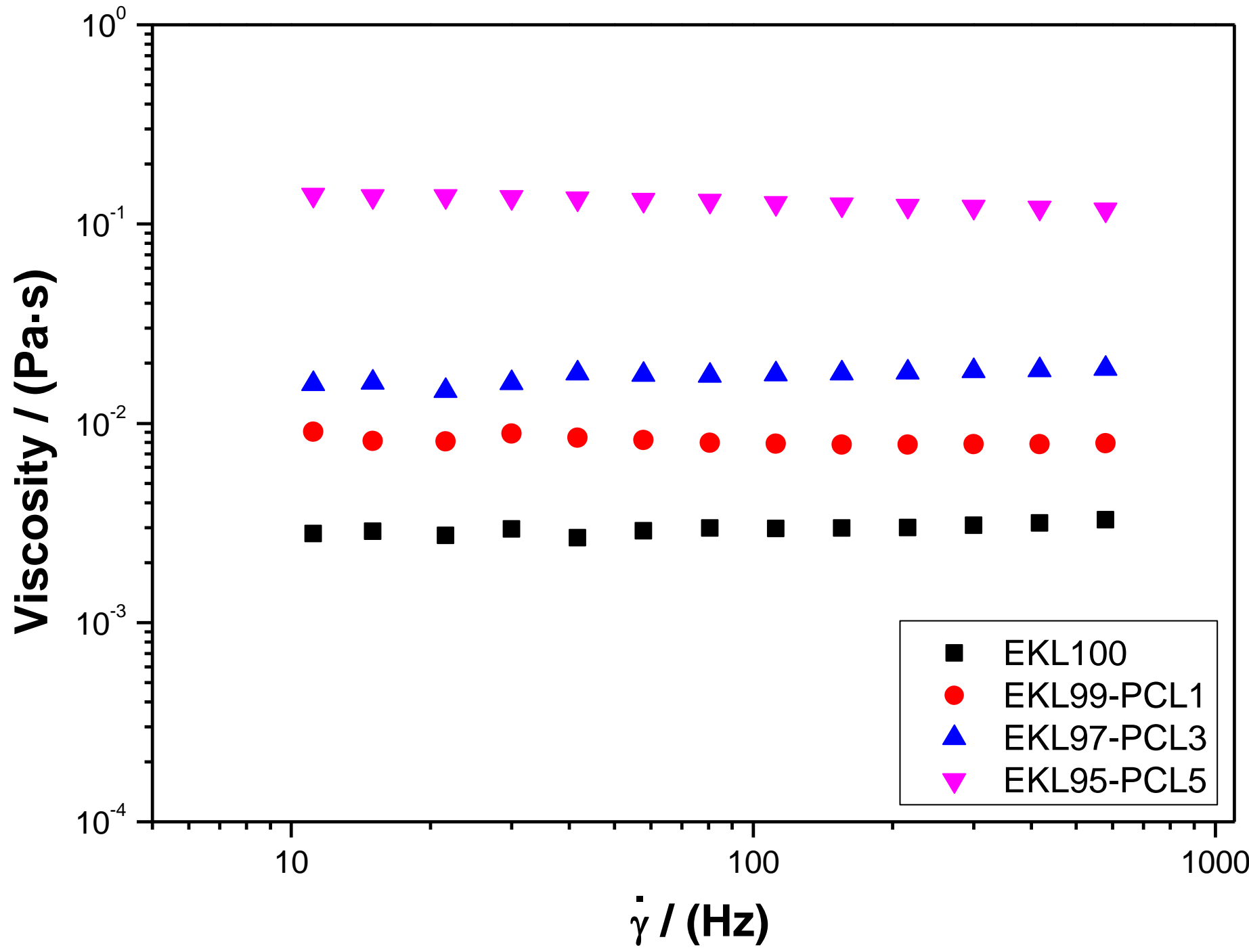


Figure 1. Viscous flow curves for EKL/PCL ratios

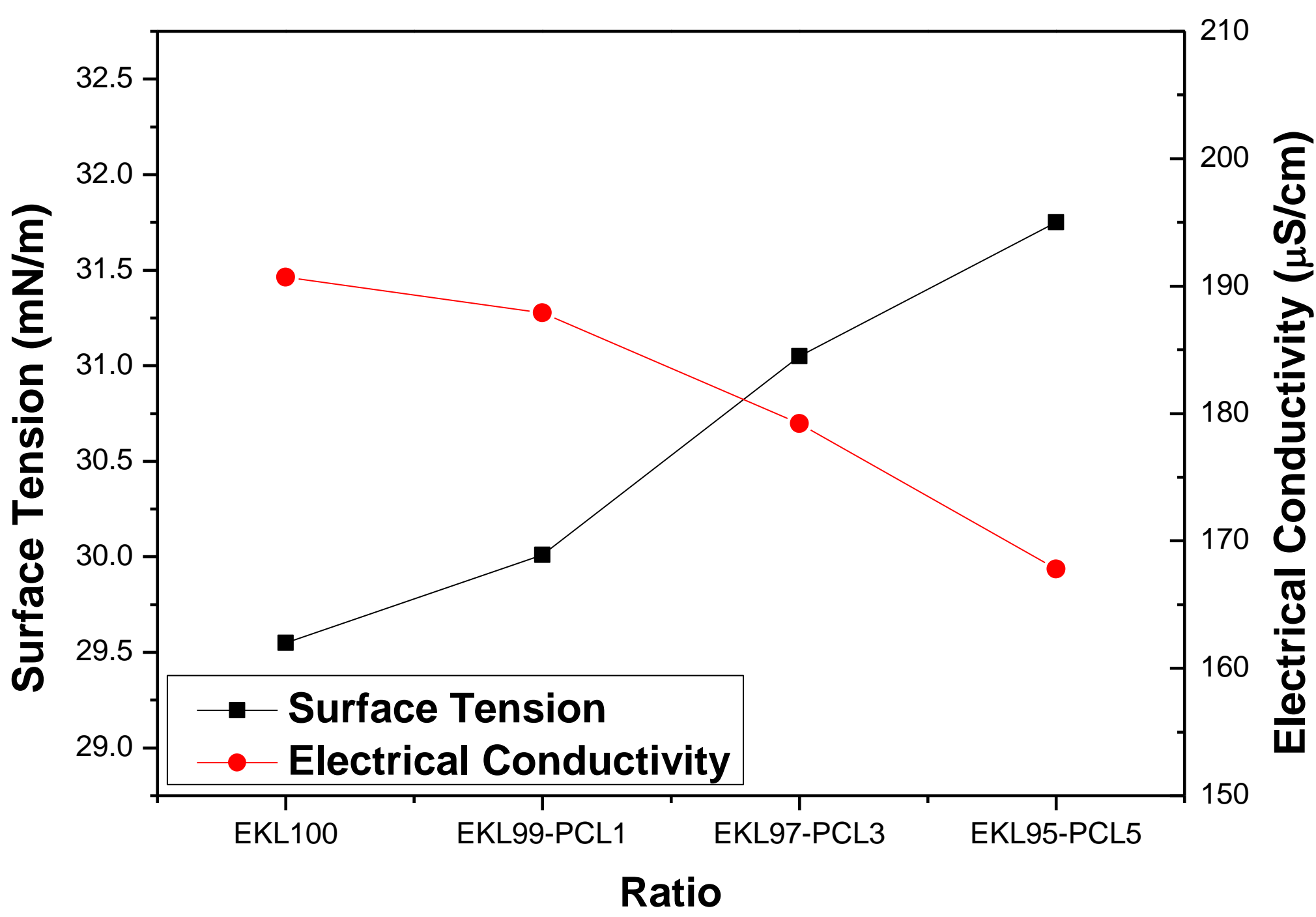


Figure 2. Surface tension and electrical conductivity vs different EKL/PCL ratios.

Table 1. Shear viscosity, surface tension and electrical conductivity for EKL:PCL solutions in DMF:chloroform. **Note.** Values with different symbols are significantly different ($p < 0.05$).

Systems	η (mPa.s)	Surface Tension (mN/m)	Electrical Conductivity ($\mu\text{S}/\text{cm}$)
EKL100	2.79 ^a	29.55 ^A	190.7 ^{aA}
EKL99-PCL1	8.85 ^b	30.01 ^B	187.9 ^{aA}
EKL97-PCL3	14.54 ^c	31.05 ^C	179.2 ^{bB}
EKL95-PCL5	109.71 ^e	31.75 ^D	167.8 ^{cC}

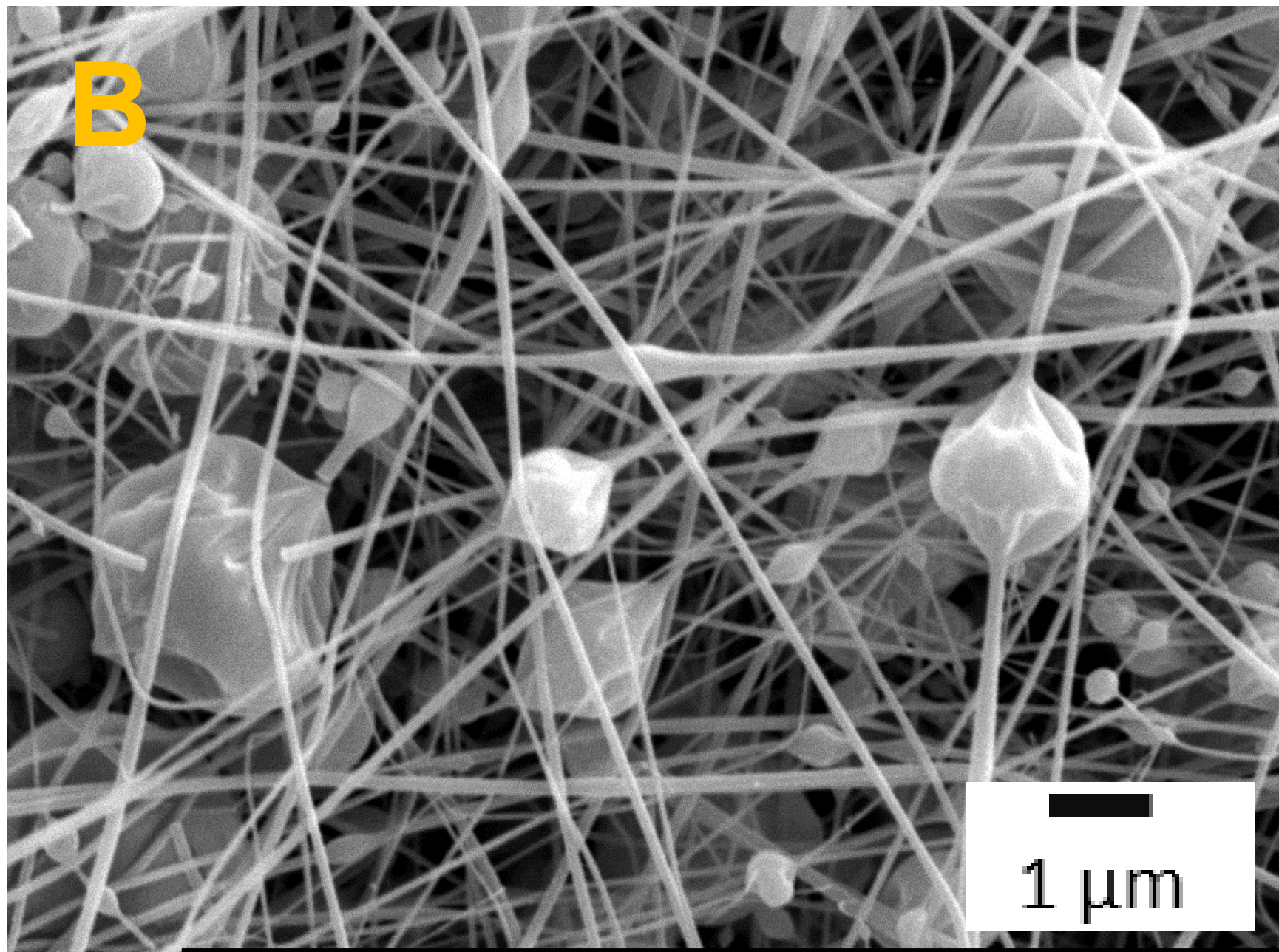
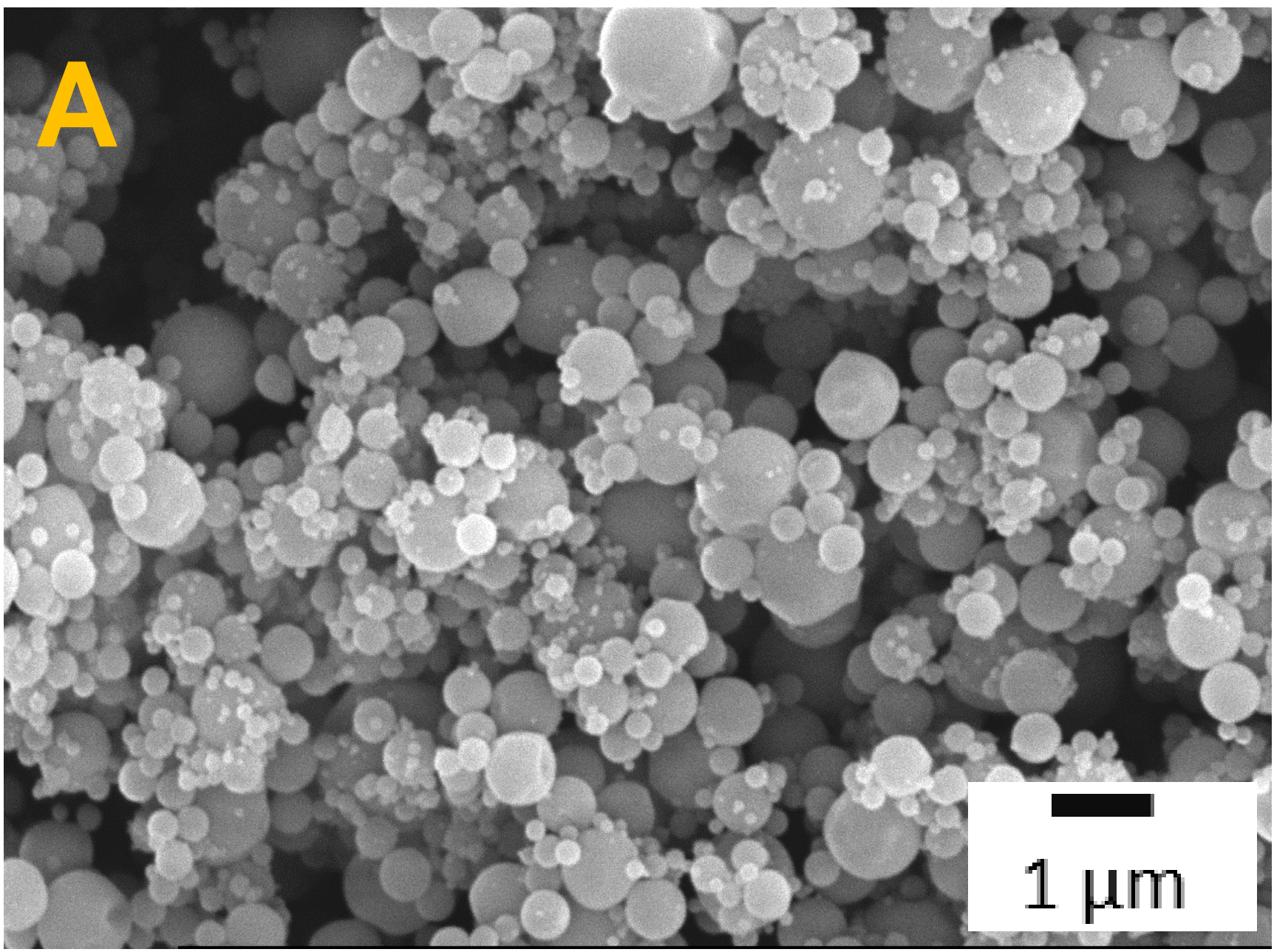


Figure 3. SEM electrospun nanostructures for A) EKL100 and B) EKL95-PCL5.

Conclusions

All EKL: PCL solutions studied exhibited Newtonian behavior over the shear range applied. Viscosity increases with PCL content. Electrical conductivity decreases with the EKL / PCL ratio and the surface tension increases with the EKL / PCL ratio. The microstructure of electrospun membranes was highly dependent on both the proportion of polymeric raw materials. This provided information on the potential of these materials for different engineering applications.

Acknowledgments

This work is part of a research project (RTI2018-096080-B-C21) sponsored by the MICINN-FEDER I+D+i Spanish Programme. J.F. Rubio-Valle has received the Ph.D. Research Grant PRE2019-090632 from MICINN (Spain). The authors gratefully acknowledge their financial support.

References

[1] Formhals, A. (1934). United States: Patent Application Publication. US patent, 1(975), 504.
[2] Sun, T., Mai, S., Norton, D., Haycock, J. W., Ryan, A. J., Macneil, S. (2005). Self-organization of skin cells in three-dimensional electrospun polystyrene scaffolds. Tissue engineering, 11(7-8), 1023-1033.
[3] Kai, D., Jiang, S., Low, Z. W., & Loh, X. J. (2015). Engineering highly stretchable lignin-based electrospun nanofibers for potential biomedical applications. Journal of Materials Chemistry B, 3(30), 6194-6204.
[4] Wang, J., Tian, L., Luo, B., Ramakrishna, S., Kai, D., Loh, X. J., ... & Mo, X. (2018). Engineering PCL/lignin nanofibers as an antioxidant scaffold for the growth of neuron and Schwann cell. Colloids and Surfaces B: Biointerfaces, 169, 356-365.