Thermal annealing induced crystallization and phase transformation in electrospun poly(lactic acid) nanofibers

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Understanding how the cellular response is influenced by the structural and mechanical characteristics of the three dimensional supporting material will drive the development of the scaffolds and devices to be used for repairmen and replacement of defective tissues [1]. Engineered biomaterials with structural, mechanical and electrical properties similar to the cellular microenvironment are a key issue to determine the eventual success or failure of such scaffolds. In this sense, it is particularly important to understand the mechanisms involved in the transmission of the mechanical forces between the cell and its supporting extracellular scaffold, that influence cell morphology and cytoskeletal organization phenotype and tissue engineering [2]. The ability to probe such interactions is fundamental to design improved biomaterials with enhanced functionality and specificity.

An ideal tissue engineered scaffold should be mechanically stable and capable of perform biologically in the implant location. The mechanical stability is an intrinsic property of the selected material, the architectural design of the scaffold and the material interactions. Biologic functioning is regulated by biologic signals from growth factors, extracellular matrix (ECM) and surrounding cells. ECM molecules surround cell to provide mechanical support and regulate cell activities [3].

Electrospinning is method for the fabrication of flexible and highly porous nanofiber scaffolds by applying a high electric field to a droplet of polymer solution or melt. When the diameter of the polymer fibres are shrunk from micrometers to sub-microns or nanometers, there appear interesting characteristics such as very large surface area to volume ratio, flexibility in tailor-made surface functionalities and superior mechanical performance compared with any other known form of the material.

Scaffolds of biodegradable polymers like poly(lactic acid) (PLA) find numerous applications in tissue repair and regeneration. The tissue engineering approach relies upon the use of polymer scaffolds, which is used as support for cell adhesion, proliferation and differentiation, providing them with mechanical reinforcement until the regenerated tissue is able to sustain the applied forces “in vivo”. Scaffolds also help to the organization of the produced ECM. Growth of cells on a polymeric scaffold using the principles of tissue engineering provides a viable “in vitro” model for biological experimentation.

In this work, it is reported how thermal annealing can induce tailored crystallinity and phase content to the electrospun nanofibers (figure 1a). The evolution of the mechanical properties of the nanofibers is correlated to the morphology, degree of crystalline degree and specific phase content. The infrared and differential scanning calorimetry measurements reveal that the PLLA electrospun scaffold crystallizes into α-crystals with the distorted 10_3 helix conformation from solution, with a degree of crystallinity around 9 %.

Annealing of the samples has been performed at temperatures from 40 to 140 ºC and times from 1 min to 48 h. The bands at 955 cm^{-1} and 871 cm^{-1} related to the amorphous and crystalline phases [4], respectively, of the PLLA fibers, remain quite similar for the samples annealed at 40 ºC for times up to one hour, increasing the crystalline phase related bands for higher annealing times. Annealing at higher temperatures, i.e. 70 ºC (above glass transition temperature), 90 ºC and 120 ºC, results predominantly in α-phase crystals. Overall, the crystallinity variation of the samples can be from ~ 9 % for a non-annealed sample up to a maximum of ~30 %. Further, high temperature annealing at 140 ºC for 48 h induces the appearance of the β-phase of the material, as demonstrated by the band that appears at

908 cm^{-1} [5]. The results demonstrate that it is possible to induce phase transformation and crystallization and therefore to tailor the mechanical properties of the PLLA electrospun fibers by thermal annealing, without changing the nanofiber morphology.

In this way, thermal treatment of the PLLA electrospun scaffold enhances the biomechanical properties of the nanofibers. Moreover, the thermal annealing does not induce morphological changes, maintaining the fiber diameter and porosity of the scaffolds. This approach can be an important technique for creating grafts with better success on implantation.

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Figures

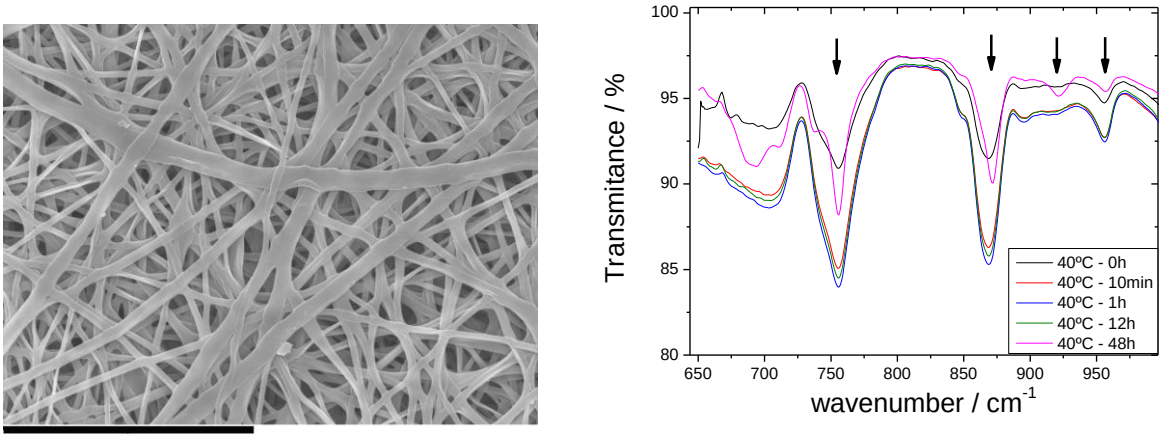

Figure 1. a) SEM microphotographs of randomly aligned (dimension bar 40 microns) PLLA electrospun nano-fibers, **b)** FTIR spectra for the electrospun scaffolds after temperature annealing for different times.