An Examination of Post-Processing Orientation in Coextruded poly (ε-caprolactone) Fibers

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Traditional methods of producing synthetic polymeric fibers include wet and dry spinning, melt spinning, and electrospinning. By utilizing melt coextrusion, typically used to produce discrete layers, the melt flow can be manipulated to produce a fiber/matrix composite in a continuous and solvent-free fashion. [1] Unlike traditional fiber processing techniques, it is possible to introduce post-processing orientation utilizing melt coextrusion, which provides a unique avenue to tune the properties of the fiber system. In this work, the fiber/matrix composite consisted of rectangular fibers of poly (ε-caprolactone) (PCL) in a poly (ethylene oxide) (PEO) matrix, which were chosen for their widespread use in the bioengineering field as tissue engineering scaffolds and for ease of surface modification on PCL fibers. Following coextrusion, the composite was washed using water and methanol to produce a nearly pure (99.2% by weight) PCL fiber system. After melt processing and composite washing, the Hermans orientation factor of the PCL fibers was ~0.01, which indicated a random crystal orientation. The fibers were then drawn at a temperature of 50 °C in order to develop an oriented crystal system. After fiber drawing (draw ratio, DR = 11), the Hermans orientation factor reached ~0.94, which indicated a highly aligned crystal phase along the fiber axis (drawing direction). [2] This drastic shift in orientation during the drawing process provides a platform to investigate *in-situ* morphology during drawing and the resulting shift in mechanical properties.

The macro/microscale and nanoscale structure of the fibers was evaluated using scanning electron microscopy (SEM) and detailed analysis of *in-situ* wide-angle X-ray scattering (WAXS). On the macroscale, it was observed that following the washing process a system of highly aligned rectangular fibers is produced. On the microscale, the dimensions (both width and thickness) of individual fibers were measured as a function of draw ratio. In the as-extruded state, the width was measured to be 2.6 ± 0.6 μm, while the thickness was measured to be 1.6 ± 0.4 μm. Following the drawing process, the fiber width was measured to be 0.31 ± 0.05 μm and the thickness was measured to be 0.13 ± 0.02 μm. It was observed that a linear relationship exists between the fiber dimensions and draw ratio, suggesting that the fibers undergo affine deformation and demonstrating the ability to control fiber dimensions through post-processing orientation. Scherrer WAXS analysis revealed that PCL crystallites are fragmented into smaller crystallites during the drawing process. [3] Following the orientation step, the fibers were cooled down to room temperature and in the process, pass through the crystallization temperature of PCL, and the crystallinity increased from roughly 40% in the as-extruded state, to almost 60% in the oriented state. Based on these investigations, a complete picture of the macroscopic, microscopic, and nanoscopic hierarchical structure formed within the coextruded PCL fibers was developed using advanced X-ray scattering techniques and microscopy imaging.

In the second part of the study, we explored the thermo-mechanical properties of the as-extruded fibers and the oriented fibers to correlate the observed structure to the properties developed. A comparison of the melting endotherms of the first heating differential scanning calorimetry (DSC) thermograms revealed that the melting enthalpy of the oriented fibers was substantially higher than that of the as-extruded fibers, which agrees with the higher crystallinity estimates obtained from WAXS. Additionally, the melting endotherm of the oriented fibers was more well-defined than that of the as-extruded fibers, shifting to a slightly lower melting temperature, which is consistent with smaller individual crystallites that are also observed in

WAXS. The dynamic mechanical properties and tensile properties of bundles of as-extruded and oriented fibers were also examined, revealing a 10x increase in storage modulus (dynamic mechanical analysis measurements) as well as a 10x increase in tensile strength and 30x increase in tensile modulus (uniaxial tensile measurements). The extreme enhancement in the mechanical properties of the oriented fiber bundles was attributed to the shift from large, randomly oriented crystallites to smaller, highly ordered crystallites.

In order to assess the viability of replacing traditional electrospun fibers with extruded fibers, electrospun fibers of comparable diameter to those of the extruded fibers were produced and the thermal and mechanical properties of both systems were investigated. As-extruded, rectangular PCL fibers compared well to electrospun, circular PCL fibers with similar mechanical behavior, while having a surface area roughly 30x higher than conventionally produced electrospun fiber mats. The oriented PCL fibers significantly outperformed electrospun fibers, exhibiting higher storage modulus, tensile modulus, and tensile strength (Figure 1). Finally, a facile method of solvent and PEO recovery was developed to reduce waste generated during fiber production.

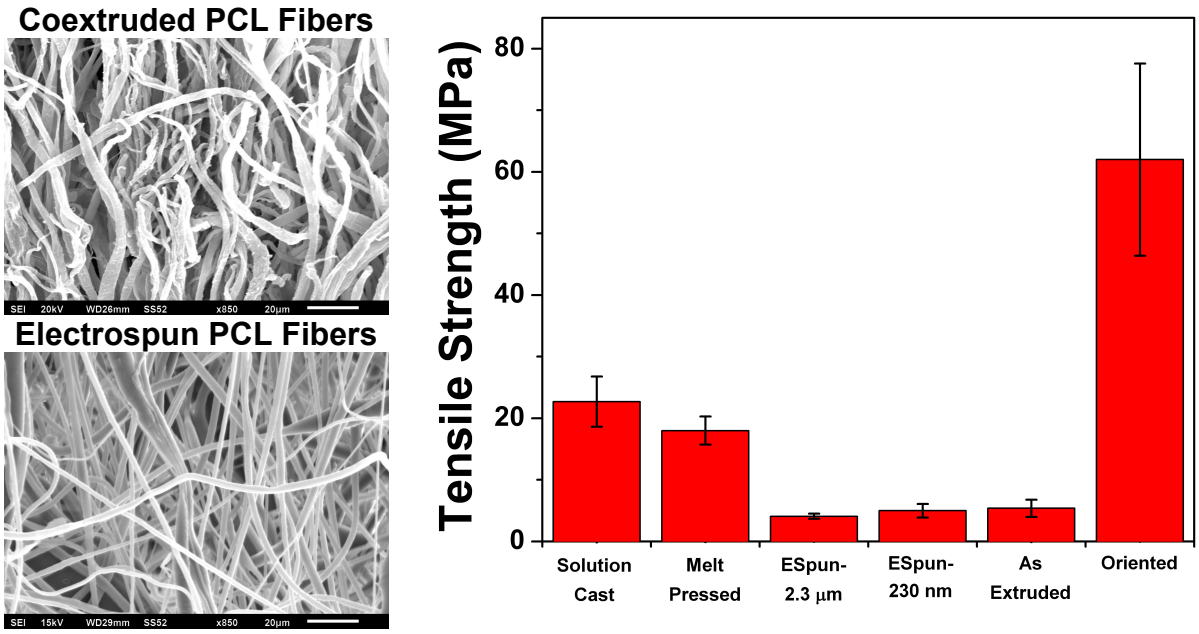


Figure 1. *SEM micrographs of As Extruded and ESpun-2.3 μm PCL fibers with plotted tensile strength of solution cast and melt pressed PCL mats, electrospun, as extruded and oriented PCL fibers.*

References

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