Electrospinning of PVDF-based copolymers

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Electrospinning is a versatile technique for the fabrication of fibers with nano- or microscale size from polymer solution or melt through electrostatic forces. Electrospun membranes are attracting significant attention in plenty of applications, such as tissue engineering, energy conversion, filtration, sensing systems, and protective clothing [1]. Polyvinylidene fluoride (PVDF) is one of the most studied polymers for electrospinning due to its fascinating physico-chemical and electrical properties, such as hydrophobicity, piezoelectric, pyroelectric, and ferroelectric characteristics [2]. Depending on the chain conformation, PVDF shows five distinct crystalline polymorphs, among which the *β*-form is the most intriguing thanks to its extraordinary piezo, pyro and ferroelectric properties due to the zigzag *all-trans* conformation. Interestingly, electrospinning can induce the *β*-phase formation during the fabrication process, without need of post processing [3]. Moreover, the nanostructure obtained by electrospinning can further promote the PVDF hydrophobicity. Finally, the introduction of selected comonomers allows to finely tune the final properties of the fluorinated material.

In this work, electrospinning process of PVDF-based copolymers, namely poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-trifluoroethylene-hexafluoropropylene) (PVDF-TrFE-HFP) and poly(vinylidene fluoride-trifluoroethylene-2(trifluoromethyl)acrylic acid) (PVDF-TrFE-MAF), was investigated. The effect of the PVDF comonomer on the fabrication of fibrous membranes and their final properties was studied, and a comparison with flat casted films was assessed. Electrospinning conditions were optimized by varying solution concentration, working distance, applied voltage, and flow rate. Fibrous membranes (Fig. 1a) were successfully fabricated with all the investigated copolymers and their morphology was characterized by FE-SEM. The mat crystallinity was monitored by DSC, while FT-IR and XRD analyses demonstrated the enhancement of the *β*-phase content in the fibrous membranes (Fig. 1b). Furthermore, the electrospun samples showed higher hydrophobicity than the flat films (Fig. 1c). Thanks to their properties, the fluorinated fiber mats can thus be promising as flexible electroactive membranes or water/oil separation filters.

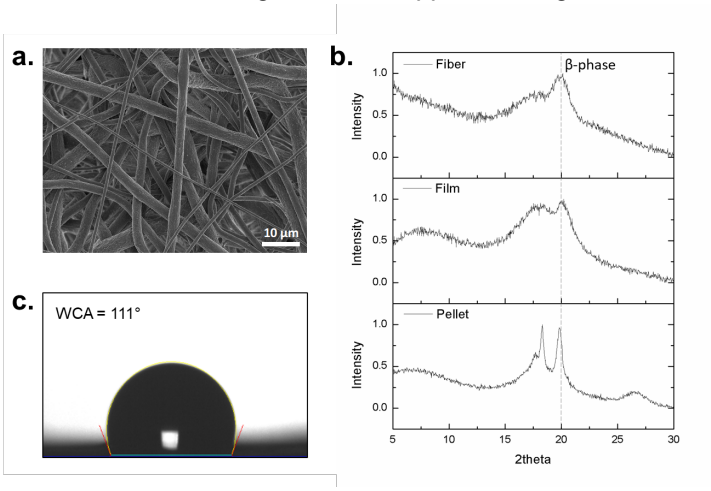

Fig. 1: a. PVDF-HFP electrospun membrane, b. XRD spectra of PVDF-HFP, c. water contact angle of a PVDF-HFP fibrous membrane.

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