Mechanical properties on electrospun polymeric membranes: AFM measurement methods.

Violeta Hurtado-García[1,2,3] [0000-0003-2731-538X], Javier Pinto[1,2,3] [0000-0003-3155-8225], Suset Barroso-Solares[1,2,3] [0000-0002-2311-1905]

[1]Cellular Materials Laboratory (CellMat), Condensed Matter Physics, Crystallography, and Mineralogy Department, Faculty of Science, University of Valladolid (Spain).

[2]BioEcoUVA Research Institute on Bioeconomy, University of Valladolid (Spain).

[3]Study, Preservation, and Recovery of Archaeological, Historical and Environmental Heritage (AHMAT) Research Group, Condensed Matter Physics, Crystallography, and Mineralogy Department, Faculty of Science, University of Valladolid (Spain).

violeta.hurtado@uva.com

Abstract. Electrospun polymeric membranes, crucial in industries like water treatment, biomedical engineering, and gas separation, rely on their mechanical properties, including tensile strength, elasticity, and durability, for effectiveness and longevity. Optimal mechanical properties enable those membranes to withstand pressure fluctuations, aggressive chemicals, and various usage cycles, enhancing operational efficiency and sustainability. The tunability of these properties is key to customizing membranes for specific applications. In this regard, Atomic Force Microscopy (AFM) has proven its efficacy in the nanomechanical characterization of soft materials over the past two decades. This work reviews recent literature on AFM methods to measure mechanical properties in electrospun materials, discussing their potentialities and current applications.

Keywords: electrospun polymeric fibers, mechanical properties, AFM.

1 Introduction

The mechanical properties of polymeric membranes are crucial due to their wide range of applications in various industries, including water treatment, biomedical engineering, and gas separation [1]. These mechanical properties, such as tensile strength, elasticity, and durability, determine the effectiveness and lifespan of the membranes under actual operational conditions. A membrane with optimized mechanical properties can withstand pressure fluctuations and aggressive chemicals, ensuring efficient and sustainable operation and resisting different cycles of use and washing [2]. Furthermore, the adaptability of these properties allows for the fabrication of customized membranes for specific applications, thereby enhancing their performance and efficiency [3]. Research and development in this field improve the quality and functionality of polymeric membranes and contribute to technological advances in critical areas such as environmental sustainability and human health.

Fibrous polymeric membranes have emerged as innovative materials in various industrial, technological, and scientific applications. Historically, the development of these membranes has been driven by the need for synthetic textiles [3], but it was quickly noticed that the possibilities offered by these materials could be extended to a wide range of applications. This emergence is attributed to a unique combination of properties. Selective permeability, substance delivery properties, fouling resistance, chemical and thermal stability, or the emergence of anisotropic properties are some of them. Coupled with versatility in manufacturing materials, their low cost and ease of manufacture make them advanced, high-performance materials in many applications [1]. Efficient and economical separation processes in diverse fields ranging from desalination and oil-water separation [4] to gas separation [5]; biomedical applications like wound dressings, drug delivery, and tissue scaffolding [2]; as well as in sensors [6] and energy storage [7] are the most important ones.

In terms of mechanical properties, polymeric membranes significantly enhance them compared to their solid counterparts in relation to their relative density [8,9]. Their small cross-section and large aspect ratio (ratio of length to diameter of a fiber) give them greater flexibility and tensile strength, making them suitable for applications where mechanical resistance is crucial [10]. Furthermore, manipulating the membrane morphology at the nanoscale further improves these properties, thus optimizing their performance under demanding usage conditions [11].

Electrospinning has gained popularity in polymeric fibers due to its cost-effectiveness, efficiency, and large-scale production capability [3]. Fibrous membranes made by electrospinning could reach a few tens of nanometres in averaged diameters, displaying a great specific surface area [5]. Also, they exhibit abundant microstructures, offering significant advantages over other membrane fabrication techniques [3]. In terms of mechanical properties, nanofibrous structures have higher mechanical strength than larger fibers [8]. Therefore, a technique such as electrospinning, capable of producing fibers so thin, becomes relevant in the control and improvement of mechanical behaviour.

Furthermore, electrospun membranes demonstrate significant anisotropy, meaning their properties vary depending on the measurement direction. This anisotropy is particularly relevant in applications where the direction of applied forces is critical, such as pressure sensors [12], or when they must withstand stresses in a preferred direction, such as in wound dressings or tissular scaffolds [13]. On the other side, the need to control and enhance the mechanical properties of these membranes is crucial in medical and biological applications, where the dressings must emulate the mechanical properties of the skin or other tissues [14]. Also, it is necessary in filtration applications, where specific resistance to washing cycles and stability against physical degradation are required [3].

Given the wide range of critical applications of polymeric membranes, precisely measuring their mechanical properties is paramount. This necessity is especially crucial when considering individual fibers, as their specific characteristics significantly influence the overall material performance. Atomic Force Microscopy (AFM) emerges as a fitting technique for this purpose: it offers the required precision and detail at the nanoscale to produce not only punctual measurements but also nanomechanical testing maps of the fiber surface [14]. Also, the AFM tip can perform micrometrical bending tests of isolated nanofibers[15].

The present work is focused on summarizing the main features of Atomic Force Microscopy (AFM) technique and its various modes for measuring mechanical properties in soft matter as electrospun fibers, including a review of the latest studies performed with each technique.

2 AFM methods on the characterization of electrospun fibers.

The mechanical properties of the fiber mats or membranes strongly depend on the measurement technique, whether performed at the nanometer scale, on an individual fiber, or at the macroscopic scale [16]. Macroscopical evaluation of electrospun mechanical characteristics on mats typically involves using a standard tensile tester [17]. The results reflect the overall macroscopic properties of the materials, which are significantly influenced by their microscopic attributes (e.g., fiber diameter and crystallinity) [18] and macroscopic features (e.g., porosity and fiber orientation) [19]. It is usually an easier measurement than the characterization of individual fibers, but data interpretation could be difficult due to inhomogeneities on the mat [16]. Moreover, the information obtained is about the material as a whole, not about its individual components.

Knowledge of the mechanical properties of individual fibers allows a bottom-up approach to the design of fiber mats. Such measurements enable the optimization of manufacturing parameters to produce materials with precise properties [16,20]. Finally, equipment with a high spatial resolution (10-100 nm) and the capability to measure in the sample's environment is required to characterize individual fibers at the nanoscale [21].

In this regard, the atomic force microscopy (AFM) meets these requirements. AFM has successfully contributed to the nanomechanical characterization of soft matter in the last two decades [22,23], reaching remarkable results in the characterization at nanoscale resolution of polymer interfaces in their native state [24].

AFM is a mechanical microscope that turns the force acting between an ultra-sharp tip and a sample surface into the displacement of a cantilever-tip transducer [25]. It allows for registering force-distance curves, different parametric variations, and topological images of the sample surface [26]. There are two wide operating methods according to the cantilever movement: on-resonance and off-resonance ones [27]. In on-resonance methods, the cantilever is excited at its fundamental resonance. The amplitude and phase shift of the resonance oscillation (the observables) will be affected by the interaction forces between the tip and the sample, and these changes are recorded. In off-resonance methods, the cantilever is excited at a frequency much smaller than the fundamental resonance. Meanwhile, its deflection is recorded. Force-distance curves, essential parameters of the tip's measurement, and the scheme of both methods are reproduced in Figure 1, courtesy of R. García, [24].

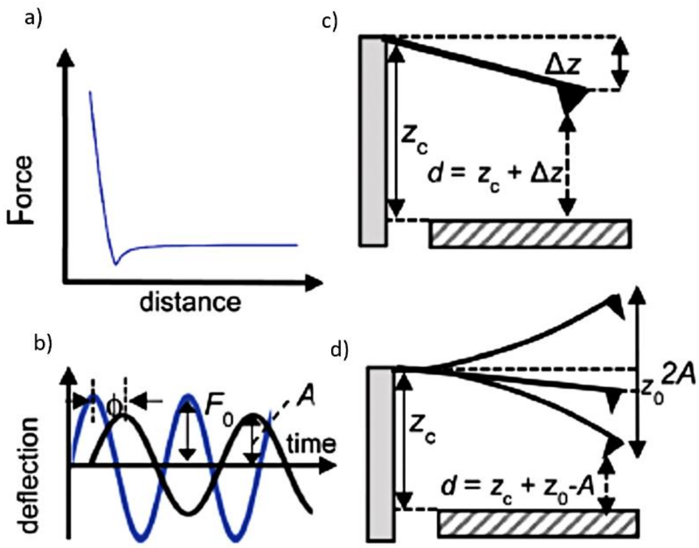

Fig. 1. a) Force-distance curve b) Driving force (blue) and tip's oscillation in the presence of a force (black). Definition of phase shift, Φ. c) Scheme of the distances and deflections in an **off-resonance** AFM measurement. z_C is the probe-surface separation; d is the closest approach of the tip to the sample surface; z_0 is the average tip deflection. d) Scheme of the distances and deflections in an **on-resonance** AFM measurement. A is the amplitude of the oscillation. Both images adapted from ref. [24], Creative Commons Attribution-Non-Commercial 3.0. Unported License.

Regarding measuring soft matter's mechanical properties, such as fiber membranes and individual fibers, AFM methods can be divided into two big families: parametric methods and force-distance curves (FDC) [24]. In this work, this classification will be followed to group different AFM-based techniques on fiber characterization. In parametric methods, an analytic model calculates mechanical properties from the observables. They are all on-resonance methods, and the excitation and detection of the cantilever deflection is performed at one or several of its resonance frequencies or at a multiple of the fundamental one [24]. This group has techniques such as amplitude modulation (AM-AFM, also called tapping mode), torsional harmonics or bimodal AFM [24].

On the other hand, FDC provides the dependence of the force between the tip and the surface at each point on the surface [22]. This approach can be performed both in an on-resonance and off-resonance way. Mechanical properties are extracted fitting the resulting FDC to a contact mechanics model [27]. Techniques as Force-volume (FV) and Peak Force Quantitative Nanomechanical Mapping (PFQNM) are the most common in this group [29].

In addition to these methods, another different approach using AFM has been performed to characterize only individual fibers [28,30–32]. It uses the cantilever as a micro-bending [31] or micro-tensile tester [15]. The fiber must be suspended and anchored at the ends to a support like a grid [30] (see Fig.2 a). Then, the cantilever-tip system is used to stretch or bend the fiber, while the stress and strain are registered. This method is equally named in the literature as AFM bending [31] or AFM-optical microscopy [15], the latter due to an optical microscope must be coupled to the AFM to monitor the process constantly. It is the exact measurement type achieved with a nanomechanical tester [33].

Comparing this method with the on/off-resonance techniques, the latter can perform individual fibers tensile tests but requires complex preparation and monitoring. On the contrary, on/off-resonance techniques can measure punctual or mapped mechanical surface properties quickly and straightforwardly without any sample preparation. A summary picture of both approaches is presented in Fig. 2. A comprehensive compilation of Young's modulus of many individual polymeric electrospun fibers measured with different techniques can be found in the work of T. U. Rashid et al. [16].

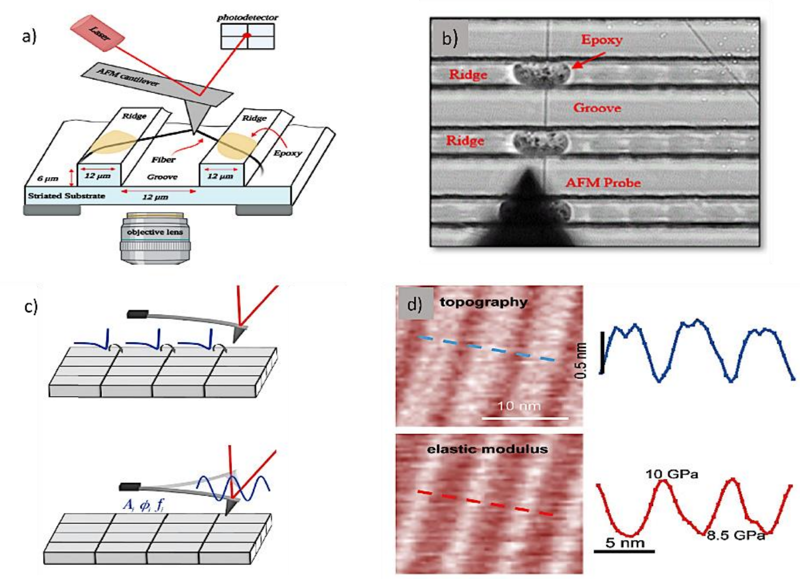

Fig. 2. Different approaches to measure tensile strength on one individual fiber: Scheme (a) and optical micrograph (b) of the experimental setup used to measure tensile strength on an individual PCL nanofiber. Both images adapted from ref. [28]. Creative Commons Attribution-Non-Commercial 3.0 Unported License. Scheme (c) and AFM micrograph, nanomechanical map and profiles (d) obtained by torsional harmonics method. The measure is performed directly on

amyloids, a nanostructured protein, a piece of soft matter like a fiber. Both images adapted from ref. [28]. Creative Commons Attribution-Non-Commercial 3.0 Unported License.

3 Last advancements on AFM fiber mechanical properties characterization.

A bibliographic review of the methods used to characterize electrospun fibers in the last five years is presented in this section, following the classification set out above.

3.1 Parametric methods

AM-AFM allows calculating punctual Young Modulus of the sample's surface by fitting amplitude-phase distance curves to theoretical models [34]. Specialized software like VEDA [35] and the more recent dForce [36] facilitate this fitting process. However, it is a time-consuming process that several techniques have improved. Advanced AM-AFM-based techniques have been developed to create AM-AFM mechanical properties maps, recently used to characterize polylactic acid (PLA) electrospun mats [37]. A summary of AM-AFM modulus of several native polymers can be found in [38].

Bimodal AFM and torsional harmonics are two parametric techniques that extract topological and mechanical properties information from separate channels. In bimodal AFM the cantilever is simultaneously excited at its first and second fundamental modes [39]. The amplitude of the first mode is used to image the topography of the surface in the same way as in amplitude modulation AFM. In contrast, the output signal of the second mode is used to map changes in the surface's mechanical, magnetic, or electrical properties[27]. Although it has good features for studying elastic properties of soft matter [40] and has been used in the study of proteins and block copolymers [41], there is no literature yet, as far as we know, applied to polymeric electrospun fibers.

Torsional harmonics involve exciting the cantilever with a driving force with both vertical and lateral components to the sample surface [27]. AM-AFM feedback is performed in the flexural direction to generate a topographic image and the force-distance curve is obtained from the torsional signal [27]. It can generate topographical and elastic modulus images simultaneously as in the bimodal case, but one advantage is that it can operate at tiny forces (~20 pN) [24]. It has been used in recent studies to measure the mechanical properties of polycaprolactone (PCL) fibers loaded with magnetic nanoparticles, demonstrating that it is a technique capable of successfully mapping the elastic modulus of the fibers and simultaneously showing the distribution of the magnetic nanoparticles [42].

3.2 FDC methods

Force distance curve methods are usually contact methods. The Derjaguin-Muller-Toporov model (DMT model) is generally applied in this type of measure to fit the experimental FDC because it considers the adhesion forces (acting outside the contact area) [27], so DMT module maps are standard outputs of FDC measurement methods. Recent studies characterize polyvinylidene fluoride (PVDF)-$K_{0.5}5Bi_{0.5}5TiO_3$ (KBT) nanofibers with this approach (see Fig. 3) [43] and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers [40].

In FV maps, an array of force measurements is obtained point-by-point in a grid pattern [44]. Nowadays, it is a high-spatial resolution technique widely used in biological characterization [45]. In samples with pronounced topography, a mismatch between the topographic and mechanical images may occur because the tip is repositioned further away to start measuring mechanical properties [29]. For this reason, electrospun fiber mats can be rugged to characterize with this technique. No recent bibliography on electrospun fibers has been found in this case.

Finally, the PFQNM method obtains force-distance curves at each sample point through controlled load-unload cycles, measuring properties like Young's modulus, adhesion, and stiffness [45]. Cuong et al. [46] characterize poly (L-lactid acid) (PLLA) electrospun nanofibers with PFQNM technique. They pointed out that the elastic modulus depends on the force applied by the tip, so it is necessary to look for the correct range in each case. Also, they underline that the optimal values are measured along the spine of the nanofiber, to avoid artefactual effects. PCL nanofibers have been also characterized with this technique [45,47], and the optimal tip for this system has been determined. According to the literature, PFQNM is a faster technique than FV [44].

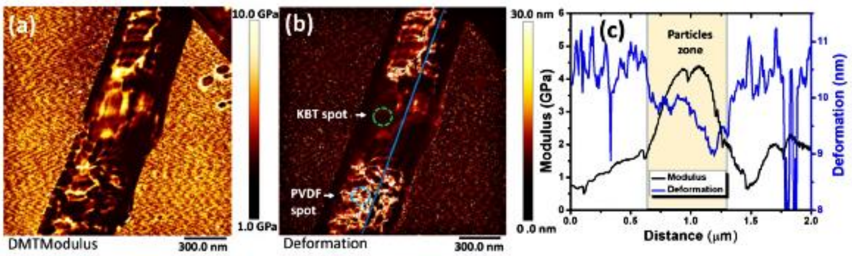

Fig. 3. PFQNM image of a PVDF-KBT fiber (a), deformation image (b) and line profile comparison between modulus and deformation along the fiber (c). The increase in modulus corresponds to the depressed zone, demonstrating that there is a KBT nanoparticle. Reprinted from [43], Copyright (2023), with permission from Elsevier.

4 Challenges and Future Perspectives

The bimodal AFM technique has been scarcely explored in electrospun fibers. Its ability to generate surface elastic modulus images at the nanoscale concurrently with topographical data makes it a promising candidate akin to torsional harmonics. Furthermore, it has already been successfully employed in studying soft matter. On the other hand, force-volume (FV) maps can also provide valuable imagery, albeit they may be more challenging to acquire due to the rugged nature of the fibers. AFM bending tests (similar to nanomechanical tests) are valuable complements when comparing surface mappings of the fiber with its overall behavior. Increasingly specific demands in medicine, sensors, substance filtration, or energy storage require precise control of the electrospinning processes, as in achieving good mechanical properties. AFM offers many valuable options to measure the elastic and viscoelastic properties of the fibers that can shed light on this area.

Acknowledgements

Financial assistance from MCIN/AEI/10.13039/501100011033 and the EU NextGenerationEU/PRTR program (PLEC2021-007705), Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04), and Ministerio de Ciencia e Innovación, EU NextGenerationEU/ PRTR program, Regional Government of Castilla y León, and EU-FEDER program "Plan Tractor En Materiales Avanzados Enfocado A Los Sectores Industriales Claves En Castilla Y León: Agroalimentario, Transporte, Energía Y Construcción (MA2TEC)" are gratefully acknowledged.

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