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Material Properties

Surface morphology and mechanical response of randomly oriented electrospun nanofibrous membrane

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ABSTRACT

Electrospinning for the fabrication of fibrous membranes has received great attention due to the simplicity of the technique, ability to effectively control the process and potential for production scale-up. While the optimization of electrospinning parameters for various polymers is widely investigated, the mechanical characterization and modeling of the mechanical response of electrospun membranes remain a major challenge. The present work focuses on the mechanical characterization of electrospun nanofibrous membrane under simple and complex loading conditions. For this purpose, polyvinylidene fluoride (PVDF) is considered for the membrane material. Three types of uniaxial mechanical tests are conducted: monotonic tensile test, cyclic loading test with increasing maximum strain and cyclic-relaxation test. The evolution of fiber re-orientation with deformation is also investigated. Results show that the membrane is initially isotropic in the plane. Moreover, the evolution of membrane Young's modulus with increasing maximum strain suggests that mechanical deformation induces two interacting phenomena: fiber re-orientation and inter-fiber bond damage.

1. Introduction

Nowadays, the advancement of technology has driven the extensive development of micro to nano-scale materials due to their improved properties as compared to the bulk materials. Among these, electrospun nanofibrous material has gained increasing attention owing to its novel physical properties such as high surface area to volume ratio, interconnected open pores, high porosity with narrow pore size distribution as well as its high water flux and permeability to gases. These highly desirable features of electrospun nanofibrous membranes lead to the in-depth investigations for a number of potential applications, such as in the filtration, distillation, separation, biomedical and drug delivery fields [1–4].

Electrospinning as a straightforward method for nanofiber fabrication utilizes a high voltage to produce ultra-fine fibers. This technique has been known for almost 100 years since it was patented in 1934 [5]. In recent years, electrospinning arises as a prominent technique for membrane fabrication due to the rapid emergence of nanotechnology that drives the worldwide interest towards the fabrication of nano-size fibers. Therefore, the optimization of electrospinning parameters is widely investigated in order to produce ideal electrospun materials suitable for implementation in various applications. The manipulation of various parameters such as polymer concentration, amount of solvent used, feed rate, voltage, and capillary-collector distance have been studied and discussed by a number of researchers in order to obtain defect-free materials with the smallest fiber diameter possible [5–11].

Limited work is available on the mechanical response of electrospun nanofibrous materials under complex loading history, despite extensive studies on the fabrication processing parameters. Although some studies exist on the mechanical behavior of electrospun nanofibrous membranes, most of the available works focused on basic mechanical properties such as tensile strength, elastic modulus and elongation at fracture, commonly obtained from monotonic uniaxial tensile tests [3,5,12–16]. Indeed, findings suggest lack of knowledge on the mechanical response of electrospun nanofibrous membranes under more complex loading histories. In fact, a thorough understanding of this mechanical behavior is always crucial in order to facilitate the design and evaluation of the material performance and degradation for industrial applications such as in water nanofiltration system and scaffolds for tissue regeneration. For instance, an ideal tissue-engineered scaffold should be mechanically stable and capable of

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functioning biologically in the implant site [17,18].

In this work, polyvinylidene fluoride (PVDF) is chosen as the raw material for the fabrication of electrospun nanofibrous membranes due to its outstanding properties that are suitable for a wide range of applications [19–21]. PVDF possesses excellent thermal and chemical stability against a wide range of harsh chemicals such as acids, strong oxidants and many organic solvents [22,23]. Consequently, the optimization of electrospun PVDF nanofibrous membrane was investigated by a few researchers [2,5,6,24]. Among these, Zhao et al. (2005) [5] obtained an optimum set of parameters for electrospun PVDF membrane, where 15 wt% of PVDF, DMF to acetone solvent ratio of 8:2, flow rate of 0.005 ml/min with 5 kV voltage were said to have produced a uniform fibrous PVDF membrane. However, Cozza et al. (2013) [6] suggested slightly different optimum parameters with DMF to acetone ratio of 7:3, flow rate of 0.003 ml/min and a voltage of 20 kV. Meanwhile, the mechanical characterization of electrospun PVDF membrane was also conducted in a few studies [3,5,12], however as mentioned earlier, only the basic mechanical properties were probed under simple loading conditions.

The main objective of this work is to propose a set of novel mechanical tests for electrospun PVDF nanofibrous membranes in order to characterize their mechanical responses under simple and complex loading histories. To this end, the membranes were fabricated using electrospinning. Two processing parameters were considered: polymer concentration and applied voltage. The resulting morphology of the membrane surface was observed using Scanning Electron Microscopy (SEM) and one representative sample with good compromise between fiber diameter and number of beads was chosen for the mechanical tests and fiber orientation analysis. The qualitative and quantitative results obtained from this work should be useful for the development of a microstructurally-motivated constitutive model describing the mechanical response of electrospun nanofibrous membranes.

2. Experimental study

2.1. Materials

Polyvinylidene fluoride (PVDF) powder with an average molecular weight of 534,000 g/mol purchased from Sigma Aldrich was used as the precursor material for membrane fabrication. Two other chemical reagents, *N*,*N*-dimethylformamide (DMF) and acetone purchased from Univar and R&M Chemicals, respectively, served as the solvents for the preparation of PVDF polymer solution.

2.2. Preparation of PVDF nanofibrous membrane

The electrospinning method was used for the fabrication of PVDF nanofibrous membranes. For this purpose, PVDF polymer solutions were prepared by dissolving PVDF powder into DMF and acetone solutions. Firstly, the desired amount of PVDF powder was dissolved in DMF and the PVDF/DMF mixture was stirred at 70 °C for 24 h. Subsequently, acetone was added and the solution was continuously stirred at 25 °C for another 24 h. Adopted from Cozza et al. (2013) [6], this technique of solution preparation that requires long term stirring processes ensures polymer and solvents to be incorporated thoroughly. The use of a co-solvent for the fabrication of PVDF membrane had been reported in a number of works, where the best fiber morphology was achieved through an optimum proportion of the two solvents [2–6]. Here, acetone as a co-solvent promoted better solvent evaporation due to its higher vapor pressure, which further reduced the chances of bead formation and the agglomeration of fibers [6]. As highlighted in the Introduction, the amount of DMF to acetone in the present study was fixed at a ratio of 7:3.

An electrospinning labscale unit from Electroris was utilized for the electrospinning. A 10 ml syringe was used as the solution reservoir where a stainless steel needle was connected as the capillary tip. The metal capillary was subsequently connected to the high voltage power supply, which can generate DC voltage up to 35 kV. The feed rate and capillary-collector distance were fixed at moderate values of 0.5 ml/h and 150 mm, respectively, for the entire investigation. Finally, a stationary grounded collector covered with aluminium foil was employed for the deposition of the electrospun nanofibers. Electrospinning was conducted for a duration of 10 h for each of the samples to obtain a considerable membrane thickness for further characterization tests.

Here, two experimental parameters were manipulated: PVDF polymer concentration and applied voltage. Two different polymer concentrations were employed, i.e. 13 wt% and 15 wt%, while three different voltages were considered for each category of solutions, i.e. 10 kV, 15 kV and 20 kV. Overall, six samples of PVDF membrane were fabricated and labelled according to their corresponding weight percentages and voltages, e.g. $P_{13}V_{10}$ for the sample fabricated from 13 wt% and 10 kV. The remaining five samples were labelled as $P_{13}V_{15}$, $P_{13}V_{20}$, $P_{15}V_{10}$, $P_{15}V_{15}$ and $P_{15}V_{20}$. Other parameters including DMF to acetone ratio, feed rate and capillary-collector distance were kept constant.

It is important to recall that the focus of this work is on the proposal of novel experimental methods for the mechanical characterization of electrospun PVDF nanofibrous membrane. In order to achieve this, fabrication of electrospun membranes is essential to provide appropriate materials for mechanical characterization (Section 2.3.2) and fiber orientation analysis (Section 2.3.3). However, the optimization of electrospinning parameters will not be investigated here since it was already reported in a number of works [7,9–11].

2.3. Characterization of electrospun PVDF membranes

2.3.1. Surface morphology analysis

The electrospun membranes were sputtered with platinum and the surface morphology of each membrane was examined with a scanning electron microscope (Phenom ProX). For the six samples, multiple images were captured under different magnifications, i.e. 1000×, 2000×, 5000× and 10,000×. Subsequently, 50 readings of the fiber diameter were manually taken in the same plane, from three different spots under a magnification of 10,000×, utilizing the measuring tools in ImageJ 1.48v software. In this case, every image that contributed to the diameter readings has the same dimension of 1024 × 1088 pixels with the same spatial resolution of 96 dpi. Moreover, only fibers located at the top surface of the images were measured to obtain accurate and consistent results. Finally, the average and the standard error of the mean of the fiber diameters were determined from the 50 readings obtained.

The amount of bead defects was evaluated from SEM images of 1000× magnification. Due to uneven bead size and bead agglomeration, the extraction of quantitative data was a daunting task. Inspired by the work of Liu et al. (2008) [25], a qualitative analysis of the amount of bead defects was utilized. Furthermore, the amount of beads was classified as “tremendous”, “many”, “intermediate”, “less” and “nil”.

2.3.2. Mechanical characterization

The mechanical response of electrospun PVDF membranes was probed using a Shimadzu AGS-X Series Universal Tensile Testing Machine equipped with a 50 N load cell. For the purpose of mechanical characterization, an electrospun PVDF membrane with the