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Structural, mechanical, and tribological properties of electrospun poly(hexamethylene adipamide) fiber mats

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ABSTRACT

The mechanical and tribological properties of electrospun fiber mats are of paramount importance to their utility in a large number of applications. In this work, mats of electrospun fibers of poly (hexamethylene adipamide) (PA 6,6) with average fiber diameter of 238 ± 22 nm are characterized for their crystal structure as well as their mechanical and tribological properties. Post-spin thermal annealing was used to modify the fiber morphology and crystallinity within the fibers. Morphological changes, in-plane tensile response, friction coefficient and wear rate were characterized as functions of the annealing temperature. The mechanical and tribological properties of the thermally annealed PA 6,6 fiber mats exhibited significant improvements through the Brill transition temperature, comparable to the improvements observed for amorphous polyamide electrospun mats annealed near the glass transition temperature. The effective wear rate of the electrospun fiber mats is well-described by a previously proposed modification of the Ratner-Lancaster relationship that relates wear to the yield behavior of these nonwoven mats.

1. Introduction

Electrospinning is a simple yet robust method to create highly porous nonwoven fiber mats from polymeric solutions. In this process, a viscoelastic fluid is charged so that a liquid jet is ejected from the surface of the fluid (typically supplied by a needle or spinneret) and accelerated by an electric field toward a collection electrode, typically a grounded plate. The resulting product is a nonwoven mat composed of fibers with small diameters (from ~100 nm to 10 μm), high specific surface area (from ~1 to 100 m^2/g), and high porosity (~90%) [1,2]. By adjusting the processing and solution parameters, the fiber diameter, porosity, specific surface area and mechanical properties of the mat can be tailored for various applications. The unique properties and relative ease of fabrication of electrospun fibers and their nonwoven mats have led to their use in a broad range of applications [3,4] including (but not limited to): degradable biomedical scaffolds [5,6], optical sensors [7], and ion-exchange membranes [8,9]. In each of these applications the mechanical and tribological response of the fiber mat is critical to the utility of the device.

Individual electrospun fibers have been shown to exhibit some remarkable increases in elastic stiffness and yield stress below a critical, submicrometer diameter, the value of which has been found to vary from polymer to polymer [10,11]; however, the origin of these increases in single fiber mechanical properties remains a topic of some debate, and may differ depending on the polymer. For non-crystalline fibers like those formed from poly (trimethyl hexamethylene terephthalamide) (PA 6(3)T), an amorphous nylon, the increases in stiffness and yield stress have been shown conclusively to result from increased molecular orientation, which in turn was attributed to increased strain during formation [11]. Regardless of the diameter-dependent changes in fiber properties, the as-spun mats tend to exhibit consistently low yield stresses (typically 0.5–3 MPa), Young's moduli (typically 20–60 MPa) and toughnesses (typically 0.5–2 MJ/m^3) [12,13]. For some applications such as tissue engineering, where a soft, porous matrix is desirable, this may be an advantage; however, for many applications of nonwoven mats, notably membranes and textiles, for example, modest improvements to the mechanical integrity without significant losses in the inherently high porosity or specific surface area would be highly desirable. Although many experimental studies have been conducted on the mechanical properties of conventional nonwoven fabrics, there are a limited number of reports that account adequately for the observed mechanical properties of mats comprising electrospun fibers [14,15]. In recent years several research groups have

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demonstrated significant improvements to the Young's modulus and yield stress of electrospun polymeric fiber mats by various forms of post-spinning techniques such as thermal annealing [16,17], mechanical drawing [18], hot pressing [19], and solvent vapor treatment [20]. For amorphous polymer nonwovens, thermal annealing has been shown to consolidate the fibers, creating stronger, more uniform materials [21]. In addition, if the amorphous polymer fiber mats are annealed above the material's glass transition temperature (T_g), flow and welding between fibers can be observed, which enhances mechanical properties through the mechanism of increased number (and perhaps rigidity) of junctions.

For a broad range of applications, nonwoven fiber materials must be not only strong, but also wear-resistant. Derler et al. have measured the friction coefficient and hardness of conventional textiles in contact with human skin equivalents [22]. Gerhardt et al. have measured the frictional properties and contact pressure of skin–fabric interactions [23]. The textile industry currently uses several abrasion and wear testing techniques (such as the Taber abraser) to evaluate the durability of fabrics. Such tribological characterization is necessary for electrospun fiber mats as well, if they are to be developed and commercialized. We have recently reported the first quantitative study of friction and wear resistance for electrospun fiber mats of the amorphous nylon PA 6(3)T. We showed that wear correlates well with the yield properties of the nonwoven mat, in accord with a modified Ratner-Lancaster model, and that significant improvements can be realized by thermal annealing in the vicinity of the polymer glass transition [17]. Here, we report the study of friction and wear resistance for electrospun fiber mats of the semi-crystalline nylon, poly(hexamethylene adipamide) (PA 6,6). The crystal structure and polymorphic phase transitions within electrospun Nylon 6 and Nylon 6,6 fibers have been previously investigated [24,25], as have the tensile mechanical properties of the electrospun Nylon 6,6 fibers [25]. Subjecting a semi-crystalline polymer fiber to heat treatment at a temperature above the glass transition temperature Tg of that polymer, but below the equilibrium melting temperature (T_m) can cause the melting of small, imperfect crystals, and the formation of larger, more perfect crystals within the fibers, thus creating a stiffer and tougher matrix [26,27]. The effect of crystallinity on the tribological properties of electrospun nonwoven mats has, to our knowledge, not yet been reported. This work reports the tribology of semi-crystalline PA 6,6 electrospun mats, correlates this with mechanical properties, and demonstrates the improvement of both mechanical integrity and wear resistance by post-spin annealing, to generate more robust membranes.

2. Experimental

2.1. Materials

Poly(hexamethylene adipamide) (Nylon 6,6), henceforth referred to as PA 6,6, was purchased from Scientific Polymer Products, Inc. It is a semi-crystalline polyamide with a glass transition temperature of 45 °C (T_g=318 K) and crystal melting temperature of 254 °C (T_m=527 K) as reported by the vendor and confirmed by differential scanning calorimetry. *N,N*-Dimethyl formamide (DMF) and formic acid (FA) were purchased from Sigma-Aldrich and used as received to create solutions with the composition 20:75:5 by weight of PA 6,6:FA:DMF. The less volatile DMF was added to prevent solidification of the solution at the needle tip and to decrease the solution conductivity.

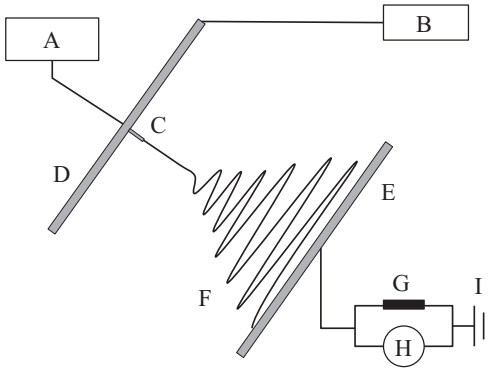

Fig. 1. Schematic representation of 45°-rotated parallel-plate electrospinning apparatus: (A) solution pump; (B) high voltage power supply; (C) capillary tip; (D) upper plate; (E) lower grounding collector plate; (F) whipping polymer fiber jet; (G) resistor; (H) voltage meter; (I) ground.

2.2. Electrospinning of fiber mats

Fiber mats were fabricated by electrospinning from organic polymer solutions using a parallel plate geometry inclined at 45° with respect to vertical, as shown in Fig. 1. Two aluminum plates (the top one 12 cm in diameter, the bottom one a 20 cm square plate) were positioned as illustrated with a tip-to-collector distance of 20 cm. The rotated geometry of the electrospinning process was employed to avoid dripping of solution onto the electrospun fiber mats, which re-dissolves the PA 6,6 fibers and disrupts the uniform fiber matrix morphology; the change in orientation should have no effect on the physics of fiber formation. A high voltage power supply (Gamma High Voltage Research, ES40P) was used to apply an electrical potential of 28 kV to the polymer solution and the top plate. The nozzle consisted of a stainless steel capillary tube (1.6 mm OD, 1.0 mm ID) (Upchurch Scientific) in the center of the top plate. A digitally controlled syringe pump (Harvard Apparatus, PHD 2000) was used to obtain a constant flow rate of 0.0023 mL/min. The entire apparatus was contained within a fume hood to ensure proper ventilation. PA 6,6 is well known to be hygroscopic, and the spinning process was found to be very sensitive to humidity. All samples fabricated for testing in this work were collected between 15% and 25% relative humidity (RH) and stored after fabrication in a sealed dry box, containing desiccant to remove any atmospheric moisture. An anti-stick agent (CP Fluoroglide® from Saint-Gobain Performance Plastics) was sprayed onto the aluminum collector plate to facilitate removal of the electrospun mat. Each mat of approximately 11–12 cm in diameter and 100 μm in thickness was produced from 0.5 mL of PA 6,6 solution.

2.3. Morphological characterization of fiber mats

A JEOL JSM-6060 scanning electron microscope (SEM), with an accelerating voltage of 10–15 kV and a working distance of 10 mm, was used to determine the diameter and morphology of the fibers. A thin layer (~10 nm) of gold was sputter-coated onto SEM samples prior to imaging. The mean and standard deviation of fiber diameter were determined based on 100 measurements of fiber diameter from a set of SEM micrographs at 17,000× magnification using ImageJ. Porosity of the fiber mats was determined gravimetrically by cutting out rectangular sections and measuring the mass and dimensions of the mat specimen and converting to porosity. Five mat thickness measurements were taken per sample with a Mitutoyo digital micrometer with a constant measuring force of 0.5 N; the mean thickness was used for porosity calculations. Lateral sample dimensions were