Measurement of Adhesion Energy of Electrospun Polymer Membranes Using a Shaft-loaded Blister Test

Shing-Chung Wong[1,*], Haining Na[1,2], Pei Chen[1]

[1] Department of Mechanical Engineering, University of Akron, Akron, OH 44325, USA
[2] Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 31520, China
* Corresponding author: swong@uakron.edu

Abstract This study aims to examine the adhesion work of electrospun polymer nano- and micro-fibers. The adhesion energy at the interface of electrospun membrane and a rigid substrate is characterized by a shaft-loaded blister test (SLBT). By controlling the processing parameters, polyvinylidene fluoride (PVDF) fibrous membranes are prepared with fiber diameters ranging from 201 ± 86 nm to 2,724 ± 587 nm. The adhesion energy between electrospun membrane and rigid substrate increases from 8.1 ± 0.7 mJ/m^2 to 258.8 ± 43.5 mJ/m^2 by use of smaller fiber diameters. Adhesion energies between electrospun PVDF membranes and SiC substrates made of different grain sizes are evaluated. Fibrous membrane produces an adhesion energy as high as 420.1 ± 62.9 mJ/m^2 in contact with SiC substrate with a 68 μm grit size. The SLBT methodology is extended to understand the adhesion energy between electrospun membranes. The increase in adhesion work is attributed to an increased area between fiber delaminated surfaces and surface asperities.

Keywords Adhesion energy, Electrospinning, Fiber diameter

1. Introduction

Hierarchical structures are usually evolved by insects and geckos on feet to produce extraordinarily strong adhesion for bodyweight support [1-3]. This phenomenon inspires researchers to use artificial polymer fibrillars in producing film-like adhesives [4-6]. Recently, thin membrane composed by ultrafine fibers is fabricated by electrospinning from polymer melt or solution [7-12] in a very simple process. The obtained electrospun membrane initiates a unique way to produce strong film-like adhesives. It requires a suitable characterization method is produced to evaluate the adhesion property of electrospun membranes.

In our previous an effective Shaft Loaded Blaster Test (SLBT) is reported to measure adhesion energy between electrospun membrane and rigid substrate [13]. As shown in Figure 1, SLBT consists of three main parts including stiff shaft, central holed rigid substrate and electrospun membrane. During SLBT, mechanical load is applied by through the stiff shaft on the center of electrospun membrane to form an axisymmetric conical delamination at membrane-substrate interface. The interrelationship of P-w_0-a between the measureable quantities, is governed by

$$P = \frac{\pi}{4}\left(\frac{Eh}{a^2}\right) w_0^{\;3} \tag{1}$$

Where P is the exterior force; E and h are elastic modulus and thickness of the membrane respectively; a and w_0 respectively refers to debonding radius and central deflection. In SLBT, mechanical equilibrium is exhibited [14-17], that is, the strain energy release rate, G, equals the work of adhesion, W, provided the entire membrane is linear elastic response. The equation is presented as

$$G = W = \frac{1}{4}\left(\frac{P\, w_0}{\pi\; a^2}\right) = \frac{1}{4\pi}\left(\frac{P}{w_0}\right)\cdot\left(\frac{w_0}{a}\right)^2 \tag{2}$$

By understanding of the principle [14-16] and process [13] of SLBT, in this paper we develop a research to discuss the adhesion work of electrospun polymer nano- and micro-fibers. Fiber diameter is systematically examined to characterize size effect of electrospun fibers on adhesion energy. Surface asperity of rigid substrate is also discussed in detail to show the condition of high adhesion energy between electrospun membrane and rigid substrate.

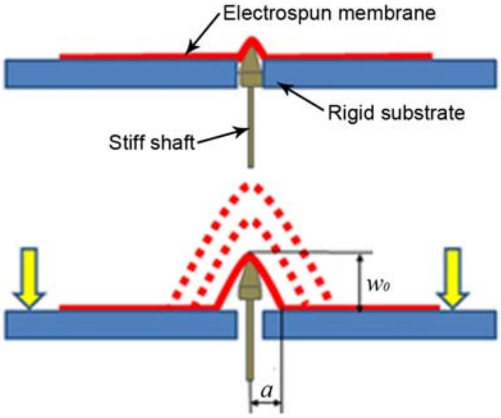

Figure 1. Schematic of shaft loaded blister test

2. Experimental Works

2.1. Materials

PVDF (Kynar 761) is purchased from Arkema Incorporation. N,N-Dimethylformamide (DMF) and acetone are purchase from Fisher Scieare at reagent grade.

2.2. Preparation of electrospun membranes

PVDF membranes for adhesion tests are fabricated by electrospinning. PVDF powder is dissolved in a solvent mixture of DMF and acetone to form PVDF solution. The concentration of PVDF solution is controlled at 0.15-0.20 g/mL. The volume ratio of DMF and acetone is selected as 7:3 and 5:5. Electrospinning is conducted at ambient temperature, solution feed rate 0.3 mL/h under applied voltage at 10 kV. Electrospinning process is proceeded ~10 h to fabricate a 10 μm thick fibrous membrane. Then electrospun PVDF membrane was dried in vacuum oven at 50 ºC for 12 h before used in SLBT.

2.3. Characterization of fiber mophology

Fiber morphology of electrospun membranes is characterized by scanning electron microscopy (JEOL JSM-6510LV). Before imaging, samples are coated with silver by sputter coater (K575x, Emitech) for 1.5 min at 55 mA. Average fiber diameter and fiber density are determined from SEM micrographs by use of the software ImageJ 1.45s. For each sample, five images are used for calculation and total 100 fibers are measured for average diameter calculation. Fiber density is also calculated by measuring the total area occupied by fibers in SEM micrographs.

2.4. Operation of SLBT

PVDF membrane is cut into a square of 30 mm by 30 mm for SLBT. The rigid substrate is prepared from cardboard with inorganic coating (detailed information of the substrate is exhibited in our previous work [13]). The arithmetic average roughness (R_a) of the substrate is approximately 128 nm. In order to make good contact, a lightweight plastic roller (~100 g) was used to roll over the membrane onto the substrate to squeeze air bubbles between membrane and substrate. Figure 1 shows a schematic of SLBT. Electrospun membrane is self-adhered onto the top surface of rigid substrate. A rigid shaft with spherical cap (R=0.35mm) is used to apply force P to the electrospun membrane. In SLBT, the test speed is consistent at 20 mm/min. Before the test, the shaft is set to just contact with electrospun PVDF membrane, but no debonding between the membrane and substrate happens. During the test, initial vertical displacement leads to a blister debonding of the local area on the membrane close to the shaft end.

In SLBT, P is recorded by a 1 N load cell (Futek Advanced Sensor Tech). The whole test is monitored by 7X-45X Simul-Focal Trinocular Boom Microscope and recorded by a 3M camera (AMscope). Video captures are analyzed by ImageJ 1.45s to obtain in-situ deformation profile. Therefore, the relationship between delamination radius (a) and central deflection (w_0) can be obtained.

Silicon carbide (SiC) substrates with different surface asperities are also used to do the SLBT to evaluate adhesion energy between electrospun membrane and rigid substrate. After the test, adhesion energy is calculated by equation (2).

3. Results and Discussion

3.1. Morphology of Electrospun Membranes

SEM images and fiber diameter of electrospun PVDF membranes are shown in Figure 2. All the electrospun membranes show uniform fibers without bead. Fiber diameter distribution is exhibited

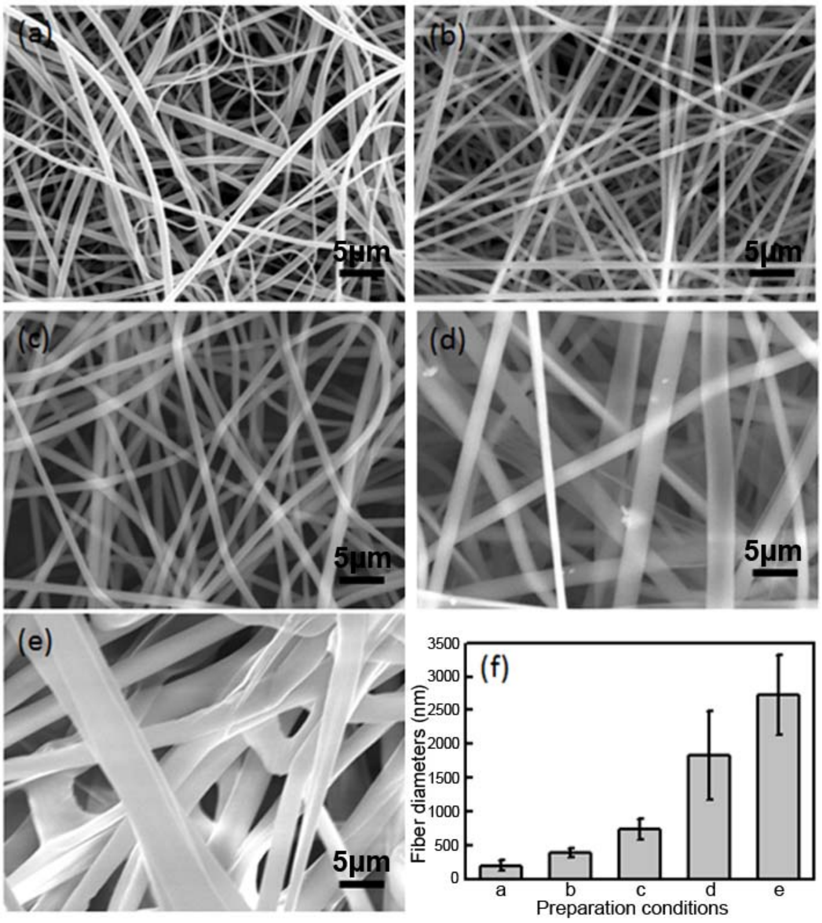

Figure 2. SEM images of electrospun PVDF membrane prepared at conditions of solution concentration and DMF/acetone (a) 0.15 g/mL, 7:3, (b) 0.17 g/mL, 7:3, (c) 0.15 g/mL, 5:5, (d) 0.17 g/mL, 5:5, (e) 0.20 g/mL, 7:3, respectively. Average fiber diameters of (a-e) is summarized at (f).

in Figure 2(f) with a trend of increase from 201 ± 86 nm to 2724 ± 587 nm. The increase of fiber diameter is attributed to high concentration of electrospun PVDF solution and large percentage of high boiling point solvent (DMF). Until today, this phenomenon is clearly recognized as the basically theory of electrospinning supported by a great deal of references [17-22]. Fiber densities of electrospun membranes are summarized in Table 1. Different fiber diameter doesn't result in different fiber density. From Table 1, fiber densities are from 77.81 % to 84.69 % without significant difference.

Table 1 Diameter, fiber density and adhesion energy of electrospun membranes

Preparation conditions	Fiber diameter (nm)	Fiber Density (%)	Adhesion Energy (mJ/m^2)
(a) 0.15 g/mL, 7:3	201 ± 86	84.7 ± 2.3	258.8 ± 43.5
(b) 0.17 g/mL, 7:3	387± 65	77.8 ± 2.8	196.3 ± 23.4
(c) 0.15 g/mL, 5:5	733 ± 154	79.2 ± 1.0	157.0 ± 37.5
(d) 0.17 g/mL, 5:5	1835 ± 653	84.7 ± 5.8	77.0 ± 8.8
(e) 0.20 g/mL, 7:3	2724 ± 587	83.3 ± 6.4	8.1 ± 0.7

3.2. The work of adhesion

The work of adhesion between electrospun membrane and rigid substrate in SLBT is calculated by equation (2) and recorded in Table 1. With the increase of fiber diameter, it shows an obvious decrease in adhesion energy. When the diameter of electrospun PVDF fibers is about 201 ± 86 nm, the adhesion energy is up to 258.8 ± 43.5 mJ/m^2. But, fiber diameter increases to 2724 ± 587 nm leading to 32-fold decrease in adhesion energy to only 8.1 ± 0.7 mJ/m^2. In SLBT, the rigid substrate has an inorganic coating on the surface indicating an arithmetic average roughness (R_a) of ~128 nm. It must form some rough area with several hundred nanometers fluctuant change on height. Because of the nano- and micro-size of electrospun PVDF fibers, they are usually very flexible with the ability to be crushed into the empty space of topographical rough area of the rigid substrate. Thin fiber is easier to produce larger effective contact with the surface of the rigid substrate. It will initiate higher work of adhesion during SLBT. On the contrary, thick fibers with the diameter of 2724 ± 587 nm are too large to be crushed into the small empty space on the topographical rough area at the surface of the rigid substrate. The contact area between electrospun membrane and rigid substrate should be very low. Low adhesion energy can be observed in SLBT.

Adhesion energy between electrospun PVDF membrane and rigid substrate is also enhanced by interlocking effect. Interlocking refers to the multi-point contact between electrospun fibers and rigid substrate. Thin fiber is no doubt flexible and easy to bend to contact many points of rigid substrate surface at the same time. The thinner electrospun PVDF fiber is, the easier the fiber forms effective contact with rigid substrate. In fact, SLBT debonding is a crack propagation process between the electrospun PVDF membrane and the rigid substrate. Formation of interlocking could increase the difficulty of crack propagation resulting in sharp increase of adhesion energy. Stein and co-workers [23] reported the sharp increase in interfacial toughness from 8 J/m^2 to 145 J/m^2 of two immiscible polymer plates by scribing grooves at the interface of plates to induce interlocking effect. By considering the flexibility of electrospun fibers and the principle of interlocking effect, it is concluded that reducing the fiber diameter of electrospun PVDF fibers is one of critical factors for significantly increases in adhesion energy between electrospun membrane and rigid substrate.

3.3. Surface roughness of rigid substrate

In order to understand the relation between adhesion energy and surface roughness of rigid substrate, a series of SiC substrates with different surface asperities is applied in SLBT to characterize adhesion energy. Figure 3 exhibits the surface morphology and surface profile of SiC substrates. All of the SiC substrates show uniform grit distribution with different grit size [see left side of Figure 3]. The smallest size of grit is 5 μm showing a height fluctuation of ~3 μm on the surface. SiC substrate also exhibits large size of grit at 68 μm with ~30 μm fluctuation on height.

Electrospun PVDF membrane with fiber diameter of 387± 65 nm is used to test the adhesion energy with SiC substrates. By increasing of the grit size on surface of SiC substrates, it shows an increase trend of adhesion energy. When the grit size is lower than 15.3 μm, the adhesion energy is below 150 mJ/m^2. By use of large grit size SiC substrate, the adhesion energy reaches over 400 mJ/m^2. At the grit size of 68 μm, it shows the highest adhesion energy at 420.1 ± 62.9 mJ/m^2.

Large size of grid produces larger empty space between the SiC grids. Electrospun PVDF fibers can

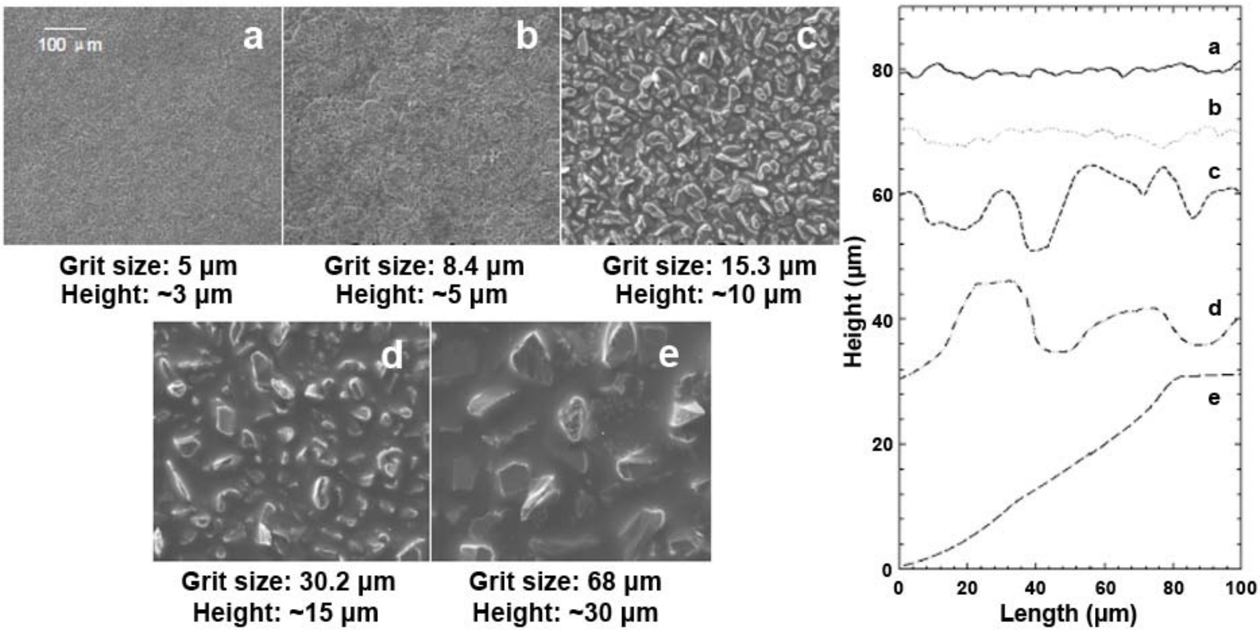

Figure 3. Surface morphology of SiC substrates.SEM images of SiC substrates (a-e) with different grit size are exhibited in left side. Surface scans of the substrate are included in right side.

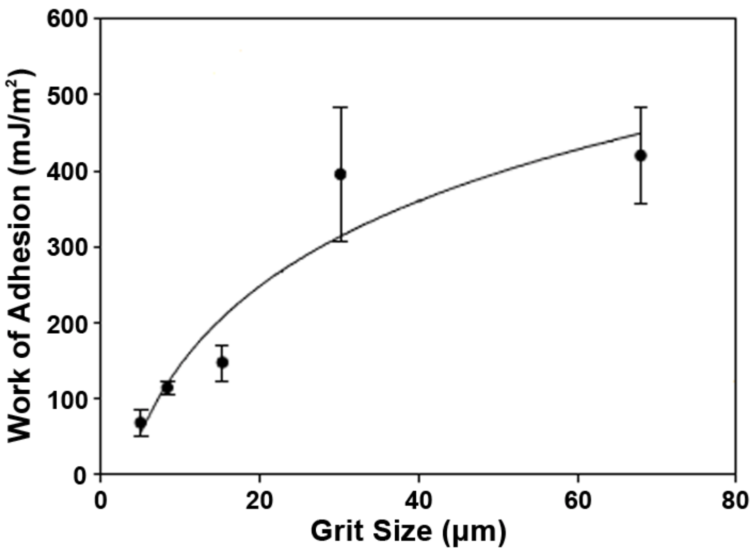

Figure 4. Adhesion energy between electrospun PVDF membrane and SiC substrate.

be easily crushed into the space to produce the high effective contact with substrate surface. When the space is large enough, many fibers can be crushed into the same area. Strong interlocking effect is initiated. As a result, higher work of adhesion can be produced in SLBT. However, when the grid size exceeds a critical value, the space between SiC grids is much larger the diameter of electrospun PVDF fibers. The increase of fiber amount will not produce an obvious increase in surface contact and interlocking effect. In our experiment, there is no large difference shown in adhesion energy between the grid sizes of SiC at 30.2 μm and 68 μm. Only 20 mJ/m^2 difference of adhesion energy is detected by use of the two SiC substrates. The surface asperity also plays an important role to the adhesion energy between electrospun membrane and rigid substrate.

4. Conclusions

SLBT methodology for testing the adhesion energy is conducted to determine the work of adhesion between PVDF membrane and rigid substrate. Electrospun PVDF membranes with increased fibers diameter show an obvious decrease in adhesion energy. The adhesion energy between electrospun membrane and rigid substrate can drop from 258.8 ± 43.5 mJ/m^2 to 8.1 ± 0.7 mJ/m^2 by increasing the fiber diameter from 201 ± 86 nm to $2{,}724 \pm 587$ nm. The surface asperity is also a critical factor for adhesion energy. The work of adhesion up to 420.1 ± 62.9 mJ/m^2 is detected between electrospun PVDF membrane and SiC substrate with a 68 μm grit size in SLBT.

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