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Procedia Materials Science 1 (2012) 13 – 18

Procedia Materials Science

www.elsevier.com/locate/procedia

11th International Congress on Metallurgy & Materials SAM/CONAMET 2011.

Adhesion Energy of Electrospun PVDF

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Abstract

Shaft loaded blaster test (SLBT) is utilized to characterize the adhesion energy of electrospun polyvinylidene fluoride (PVDF) membrane with rigid substrate in this paper. PVDF membrane prepared by electrospinning exhibits a uniform fiber morphology. At the membrane surface, the fiber diameter is 333 ± 59 nm and fiber density is roughly around 77%. When electrospun PVDF membrane is tested in SLBT, it shows full linear elastic response at the beginning. With the increase of central deflection up to 2 mm, the electrospun PVDF membrane exhibits obviously yielding. A clear yield point is observed in the debonding response curves. By analysis the elastic response of electrospun PVDF membrane, adhesion energy between the membrane and rigid substrate is calculated. The average adhesion energy is 210.1 ± 27.7 mJ/m^2.

Keywords: Shaft loaded blister test; electrospinning; adhesion

1. Introduction

Flexible polymer fibers prepared by electrospinning [Chang et al., 2010, Pu at al., 2010 and Baji et al., 2011] usually exhibits micro- or nano- dimensions. Adhesion characterization of the small size polymer fibers [Autumn et al., 2000, Gao and Yao, 2004 and Autumn et al 2002] presents new frontiers to understand naturally occurring dry adhesion [Shi et al., 2011, Qu et al., 2008 and Jeong et al., 2009]. Even though fiber adhesion plays an important role in actual application, a few approaches are considered to characterize

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 doi:10.1016/j.mspro.2012.06.003

adhesion of ultrafine electrospun fibers. Among them, almost no suitable methods were reported to test the adhesion of electrospun fibrous membrane. In this study, we use a particular shaft loaded blister test (SLBT) methodology to evaluate the adhesion energy of electrospun nonwoven with rigid substrates. The objective aims to exploit a suitable method to evaluate the dry adhesion by using polymer fibers.

SLBT is already used for testing thin membranes in terms of elastic properties as well as adhesion onto their substrate [Wang and Liao, 1999 and O'Brien et al., 2005]. Thin membranes of soft materials like polymers are usually characterized by means of this technique. In SLBT, a center holed rigid substrate is used to hold the thin membrane. The membrane locates at the center of the substrate and covers the hole. An exterior load is then applied to the membrane by a stiff shaft going through a hole in the substrate. The membrane forms a blister and exhibits mechanical responses during the test. The elastic response of the membrane is evaluated to show the energy release rate for delamination [Wan et al., 2003, Jensen, 1991 and Kozlova et al., 2008]. As to thin polymer membranes, the interrelationship between the applied force (P), central deflection (w_0), and debonding radius (a), is governed by

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

where E and h are elastic modulus and thickness of the membrane respectively. The strain energy release rate, G, equals to the work of adhesion, W, in mechanical equilibrium, which is given by [Wan and Mai, 1995]

$$G = W = \frac{1}{4}\left(\frac{Pw_0}{\pi a^2}\right) = \frac{1}{4\pi}\left(\frac{P}{w_0}\right)\cdot\left(\frac{w_0}{a}\right)^2 \qquad (2)$$

provided the entire membrane is linear elastic.

In this paper, polyvinylidene fluoride (PVDF) is electrospun into ultrafine fibrous membrane. The electrospun membrane is then used in SLBT to evaluate its adhesion with rigid substrates. By analyzing the elastic response of electrospun PVDF membrane in SLBT, the adhesion energy is calculated. To our knowledge, we made the first attempt to measure the adhesion energy of electrospun membranes. Before our research, no other suitable adhesion measurement methodology for electrospun polymers was reported.

2. Experiment

2.1. Materials

PVDF (Kynar 761) is collected from Arkema Incorporation. *N,N*-Dimethylformamide (DMF) and acetone are solvents supplied by Fisher Scientific. Rigid substrate is a high quality White Back Duplex Board (Expo India Agencies). The substrate provides a rigid top surface covered with a coating which includes high percentage nanoscale inorganic materials such as Kaolin, calcium oxide, calcium carbonate, etc. The substrate uses to mimic the flat model of inorganic material surface.

2.2. Electrospinning

PVDF powders are dissolved in 7:3 (v/v) mixed DMF and acetone at 40-50 ºC for 2 h to prepare a 0.17 g/mL solution. Then, PVDF solution is electrospun into fibrous membrane by means of single syringe electrospun setup under 8-10 kV, see left part of Figure 1. An aluminum foil wrapped flat plate is used as receptor to collect electrospun fibers. Solution feed rate is controlled at 0.3 mL/h and the distance between the needle and receptor is 8-9 cm. Ultrafine fibers forms a fibrous membrane on the receptor. After 10 h, a 10 µm thick PVDF membrane is prepared and removed from the receptor. The electrospun membrane is then dried in vacuum oven at 50 ºC for 12 h.

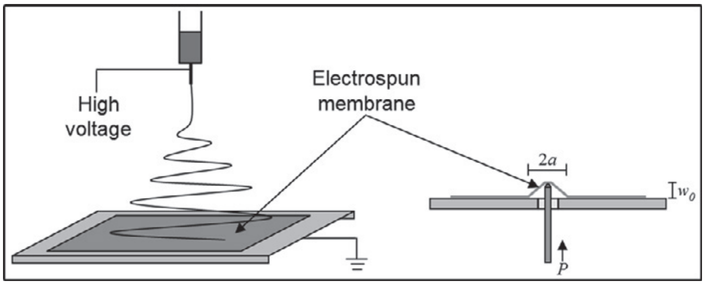

Fig. 1. Schematic of electrospinning and shaft loaded blister test (SLBT). 0.17g/mL PVDF solution is used to prepare electrospun membrane under high voltage. The obtained electrospun PVDF membrane is then removed from the receptor and used in SLBT, see left part. Exterior force is applied on the electrospun membrane by through a conical shaft thus formation of membrane blister during SLBT, see right part. The Debonding between electrospun membrane and the rigid substrate is recorded and then analyzed to exhibit the adhesive property of electrospun PVDF membrane.

2.3. Characterization

The surface morphology of electrospun membrane is firstly detected by scanning electron microscopy (Quanta 200, FEI). Electrospun PVDF membranes are coated with silver by sputter coater (K575x, Emitech) for 1.5 min at 55 mA before the test.

SLBT is carried out to characterize the adhesion between electrospun PVDF membrane and rigid substrate. As shown in the right part of Figure 1, 4 mm diameter round hole is cut through the center of the substrate. The electrospun PVDF membrane is then cut into squares of 30×30 mm and put onto the substrate. A metal roller applies mechanical pressure on the membrane for several times to exclude air pockets and to ensure intimate attachment. The substrate together with electrospun PVDF membrane is then clamped on a custom made fixture motorized by 1" actuation stage (Thorlabs, MTS 25-Z) with a speed controlled at 20 mm/min. A rigid shaft with a spherical cap with $R = 0.35$ mm is attached to a 1 N load cell (Futek Advanced Sensor Tech) to apply exterior force on the electrospun membrane. During SLBT, electrospun membrane debonds from the rigid substrate. Conical blister is formed in the center of an electrospun PVDF membrane. The debonding process is monitored by 7X-45X Simul-Focal Trinocular Boom Microscope and recorded by a 3M camera (Amscope). Simultaneous in-situ measurements of applied force (P), central deflection (w_0), debonding radius (a), and the deformation profile are measured from the video capturing debonding by Photoshop 9.0. The measurements are repeated for 5 times at different locations of the sample.

3. Experiment

3.1. Surface morphology of electrospun membrane

SEM micrograph of electrospun PVDF membrane is shown in Figure 2. The electrospun membrane exhibits uniform fiber morphology in the range of fiber diameter around 333 ± 59 nm. Fibers distribution and density are also measured from SEM image. There are about 1.81 fibers per μm on the surface. The density of the electrospun fibers is roughly 77 % and is fairly constant over the surface area. Fiber size and density endues electrospun PVDF membrane a flexible and rough surface morphology. It provides electrospun membrane the ability to produce high adhesive property with the rigid substrate.

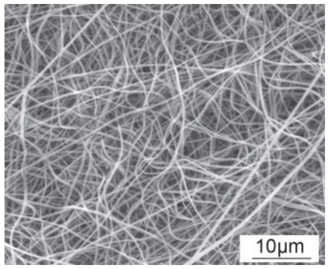

Fig. 2. SEM micrograph of electrospun PVDF membrane. Electrospun PVDF membrane is composed by flexible ultrafine fibers. At the surface, it shows uniform and well distributed fiber morphology. Fiber diameter is 333 ± 59 nm and surface fiber density is around 77%.

3.2. Shaft-loaded blister test of electrospun membrane

Even though electrospun membrane has the potential ability to show high surface adhesion in actual usage, there are still little approaches to suitably measure the adhesive property. In our research, SLBT is applied to characterize the adhesion of electrospun membrane. As schematically shown in Figure 1, a membrane blister is formed at the center of electrospun PVDF membrane in SLBT. The blister grows larger and larger. During the test, the electrospun PVDF membrane gradually debonds from the rigid substrate. Figure 3 exhibits the debonding response curves of the electrospun PVDF membrane. The relation between the external applied force (P) and central deflection (w_0) is shown in Figure 3(a). At the initial part, P-w_0 curves increase monotonically. The linear relation at the beginning justifies the assumption of elastic deformation of electrospun membrane. The elastic response is one kind of general responses of the electrospun membrane. It should include the total responses of fibers strain, the fiber elastic deformation with stretching and the fiber orientation. When the central deflection grows to 2 mm, the curve shows obvious yielding. In considering with the fiber morphology [Figure 2], the yielding of the electrospun membrane is not only related to material yielding. The yielding should be produced by the slight relative movement between fibers and the lateral slip of electrospun fiber on rigid substrate surface. Due to the amorphous fiber morphology, P-w_0 curves show an indefinite fluctuation after yielding. Further evidence of the elastic response and yielding could be found in central deflection (w_0) vs. debonding radius (a) curves, see Figure 3(b). In Figure 3(b), when central deflection is lower than 2 mm, straight trend lines are observed. With the increase of central deflection ~2 mm, the curves show obvious transition point. The nonlinear transition indicates an elastic-yielding transition behavior of the electrospun PVDF membrane in SLBT.

With the understanding of equation (2), only elastic response of thin membranes is taken into account to calculate strain energy release rate G and adhesion energy W. So, in Figure 3(a) & (b), the slopes at the initial part of the P-w_0 and w_0-a curves are measured and summarized in Table 1.

3.3. Adhesion energy

By use of the values in Table 1, adhesion energy of electrospun PVDF membrane against the rigid substrate is calculated by equation (2). The average of adhesion energy is 210.1 ± 27.7 mJ/m^2. Adhesion energy data are an energy-rate parameter defined by change in energy per unit "planar" area [mJ/m^2]. Actually it is defined in terms of "planar" debonding "area" of a membrane and does not include actual cylindrical area of individual fiber surface. Though the total actual energies derive from cylindrical contact interface and surface roughness contributes, the adhesion energy is divided by the planar area of electrospun membrane. That is to say, the adhesion energy discussion is related the whole debonding process between electrospun membrane and the rigid substrate.

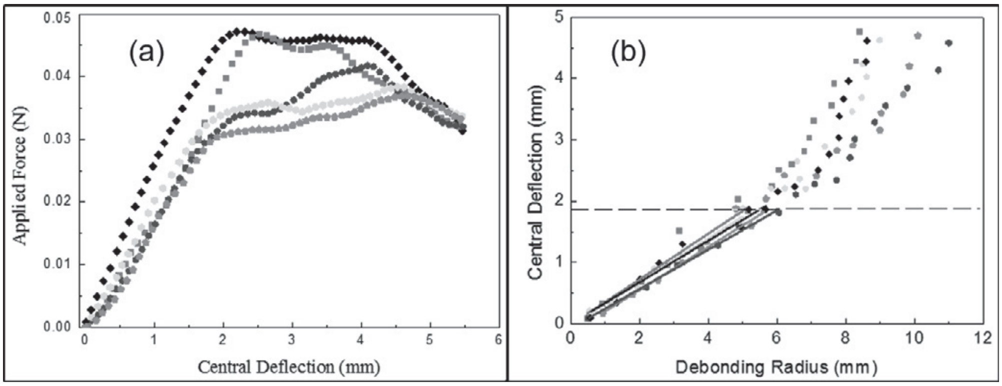

Fig. 3. Debonding response curves of electrospun PVDF membrane with rigid substrate in SLBT. External applied force (*P*) plotted as a function of blister central deflection (w_0) is given in (a). The initial parts of the P-w_0 curves show monotonic increase because of the elastic response of electrospun membrane. When w_0 is over 2 mm, the curves show obvious transition point related to the yielding of the electrospun membrane. The central deflection (w_0) vs. debonding radius (*a*) curve is shown in (b). Straight trend lines at the initial part of the w_0-a curves are easily observed. Non-linear transition points can be found when w_0 is ~2 mm. It is the further evidence for yielding of the electrospun membrane. Only the elastic response is considered to calculate the strain energy release rate and the adhesion energy. The slopes of the initial parts of P-w_0 curves and w_0-a curves are measured and summarized in Table 1 to calculate the adhesion energy between electrospun PVDF membrane and the rigid substrate.

With the understanding of the elastic deformation of electrospun membrane, the strain energy release G in equation (2) takes into full account of the strained fibers, the elastic energy associated with stretching and the fiber orientation. This thermodynamic energy balance of the SLBT is formulated in our earlier work [Wan and Mai, 1995]. The input energy comes from the applied load multiplied by the shaft displacement, $F\cdot\delta y$, and the output energy comprises fiber stretching, $\sigma\cdot\delta\varepsilon$ and creation of new surface (i.e. delamination), $\gamma\cdot\delta A$, i.e.

$$F\cdot\delta y = \sigma\cdot\delta\varepsilon + \gamma\cdot\delta A \tag{3}$$

Therefore the adhesion-delamination is purely elastic without any yielding or other energy absorption. The adhesion energy calculated by elastic response of electrospun PVDF membrane reflects the true adhesion at the membrane-substrate interface.

Table 1. Adhesion energy of electrospun PVDF membrane with rigid substrate.

Trials	P/w_0 (N/m)	w_0/a (m/m)	Adhesion energy (mJ/m^2)	Average Adhesion energy (mJ/m^2)
1	25.7	0.352	253.1	
2	22.5	0.349	217.7	
3	19.1	0.344	179.5	210.1±27.7
4	22.0	0.341	204.2	
5	22.0	0.335	196.2	

4. Conclusions

A shaft-loaded blister test is utilized to measure the adhesion energy of electrospun PVDF membrane against a rigid substrate. Electrospun PVDF membrane shows linear elastic response and obvious yielding in SLBT. Adhesion energy between electrospun PVDF membrane and the rigid substrate is obtained by analyzing the elastic response of the electrospun membrane. The average energy of adhesion is found to be 210.1 ± 27.7 mJ/m^2.

Acknowledgements

This work is supported by the National Science Foundation under a CAREER Award to SCW (NSF-CMMI 0746703). HNN is partially supported by National Natural Science Foundation of China (Project No. 51102076).

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