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Research Article

Measurement of Adhesion of *In Situ* Electrospun Nanofibers on Different Substrates by a Direct Pulling Method

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In some cases, we hope to remove the electrospun nanofibrous mesh from the collector easily. But in some cases such as wound dressing, we observe that the *in situ* electrospun nanofibers can stick to the collector (e.g., skin). Therefore, the adhesion between the *in situ* electrospun web and the substrate becomes important in the performance and practical application of the electrospun material. In this paper, we reported a direct pulling method to measure the adhesion and understand the adhesion mechanism. In this method, we used gravity to pull the fiber directly from the substrate and then measured the gravity to calculate the adhesion. This new test method is more convenient and practical than the previously reported methods. In addition, the adhesion of the *in situ* electrospun web on different substrates (e.g., aluminium foil, wood pulp paper, and silicon paper) was also studied by this method. The adhesion was influenced by spinning voltage, electrical conductivity, and surface roughness of the substrates.

1. Introduction

Nowadays, electrospinning as a simple, effective, and versatile method to produce continuous ultrafine fibers has attracted much interest in preparing various functional materials [1–5]. Thanks to the advantages of large surface-area-to-volume ratio of as-spun fibers and high porosity of the fiber meshes, electrospun fibers and meshes have shown potential applications in various fields such as nanosensors [5], filtrations [6–8], and wound dressings [9–11]. Usually, electrospun fibers and meshes were collected onto substrates, namely, collectors. For actual applications, electrospun fibers meshes might need to stick to a substrate, for example, polyacrylonitrile (PAN) onto a screen window for PM2.5 filtration [8], *in situ* electrospinning wound dressing onto the hand skin [9, 10], or removing from the collector as scaffolds for preventing hypertrophic scars [12]. Therefore, the adhesion between electrospun meshes and substrates plays a key role in the function of electrospun materials and actual applications.

Generally, the adhesion between electrospun fibers and substrates results from the van der Waals force induced by the microscale/nanoscale structures of as-spun fibers, which are characterized by high surface area-to-volume ratio, highly active chains at surface, and the electrostatic force involved by electrospinning process [13–23]. However, this kind of adhesive force is relatively weak to test. Several attempts have been reported to quantitatively measure the adhesion at microscale/nanoscale contacts, such as surface forces apparatus [24], AFM [24, 25], and indentation method [26]. However, these methods were not suitable for measuring the adhesion of meshes on a large substrate and thin membranes of soft materials like electrospun polymer meshes which contained several sheets attached to each other. To measure the adhesion of thin films like electrospun meshes, other effectively testing methods were suggested including the "dead-weight" test [16–18]; the test method is complicated to operate and the test instrument is expensive. In addition, the lap-shear test by using a Instron tensile tester

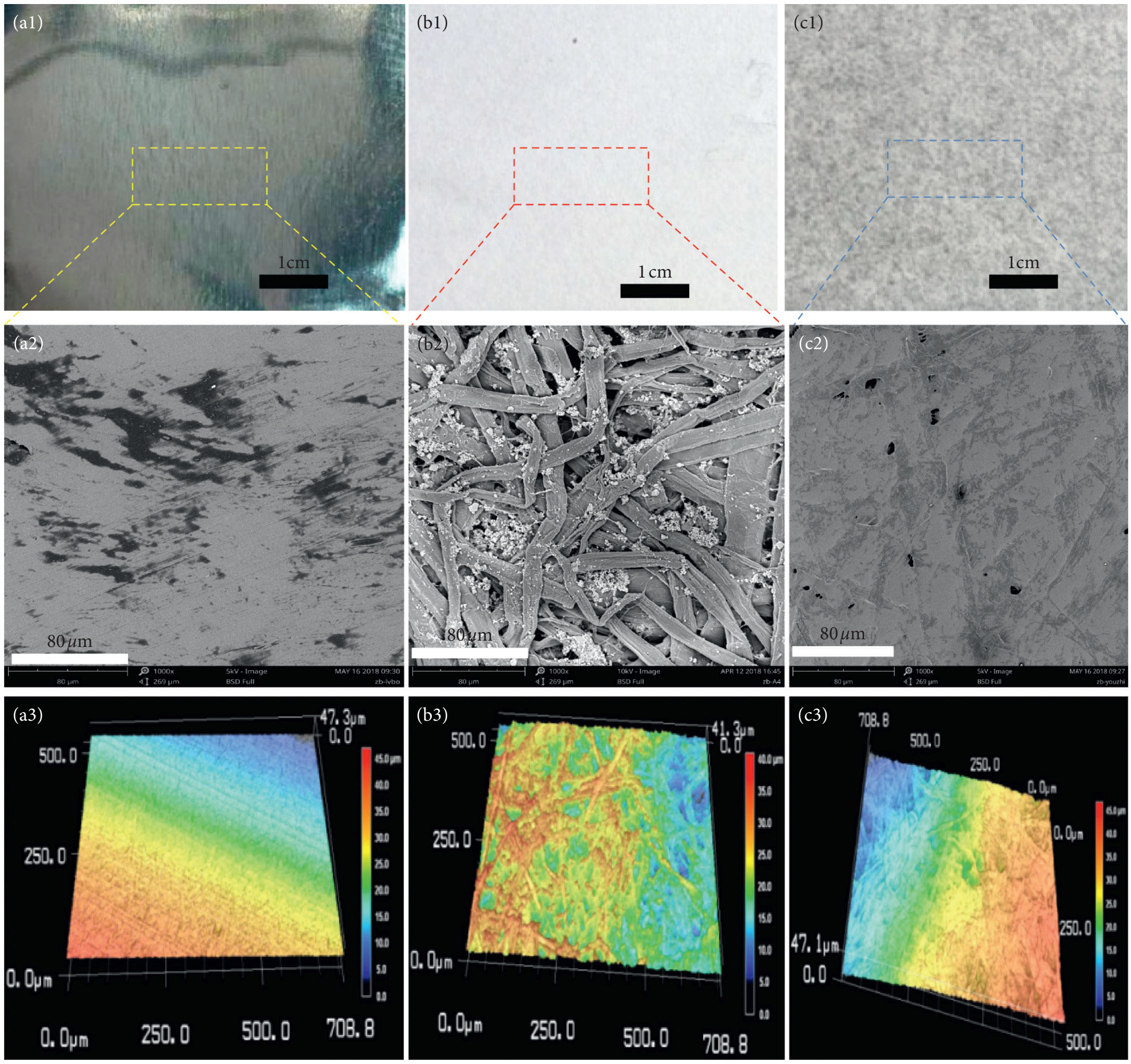


Figure 1: Optical photograph, SEM, and 3D confocal microscopy images of aluminium foil (a1, a2, a3), wood pulp paper (b1, b2, b3), and silicon paper (c1, c2, c3).

[19] and shaft-loaded blaster test (SLBT) [20–23] are complicated to operate, and it is difficult to precisely control the change in morphology between the fiber and the substrate.

Aiming to easily and quantitatively measure the adhesion between electrospun meshes and substrates, we reported a simple direct pulling method in this manuscript. Several kinds of substrates were selected and the morphologies of these substrates were examined. According to the methods in the literature [27], the morphologies of different substrates were observed as Figure 1. In the 3D figure, the yellow area in the figure is the embossment of the surface. It can be seen from Figure 2 that the surface roughness of wood pulp paper is larger than that of silicone paper and there are fibers on the surface of the wood pulp paper in the 3D morphologies. Moreover, the effects of electrospinning voltage and the morphologies of as-spun fibers and substrates on the adhesion force were discussed. These results may help to understand the mechanism of adhesion and help to find the way to strength or weaken the adhesion force for actual applications.

2. Materials and Experiment

2.1. Materials. Polyvinylpyrrolidone (PVP, 250 kDa, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in ethanol (Sinopharm Chemical Reagent Co., Ltd, China) at 13 wt.%. The solution was agitated at room temperature under constant stirring for at least 24 h before electrospinning.

Polyacrylonitrile (PAN, 250 kDa, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in *N*,*N*-dimethylformamide (Sinopharm Chemical Reagent Co., Ltd,

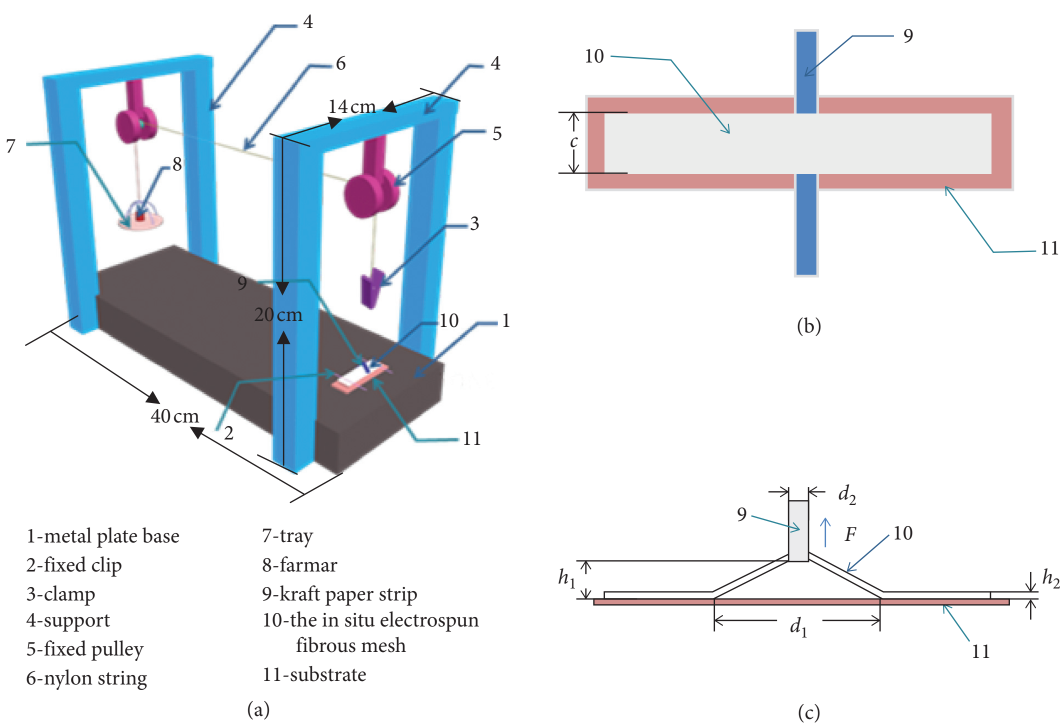


FIGURE 2: (a) The schematic diagram of the direct pulling apparatus for adhesion measurement. (b) Detail drawing of the substrate showing that nanofibrous mesh (with width of c) was electrospun onto a substrate and a kraft paper strip was set between the as-spun mesh and the substrate. (c) A force (F) was applied on the electrospun membrane by pulling the kraft paper strip, thus forming a trapezoid shape and the bottom, and upper side length (d_1 and d_2) as well as the pulling height (h_1) and thickness of the electrospun mesh (h_2) were recorded and analyzed to obtain the adhesion force.

China) at 17 wt.%. The solution was agitated at room temperature under constant stirring for at least 24 h before electrospinning.

Thermoplastic polyurethanes (TPU, 250 kDa, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in *N*,*N*-dimethylformamide (Sinopharm Chemical Reagent Co., Ltd, China) at 30 wt.%. The solution was agitated at room temperature under constant stirring for at least 24 h before electrospinning.

Aluminium foil (purchased from Meijia Chufang), wood pulp paper (70 $g{\cdot}m^{-2}$, PT. Riau Andalan Kortas), and silicon paper (Art Exhibition, purchased from Shanghai Qiner Packaging Technique LTD.CO) were selected as substrates, which may exhibit conductive, insulating, and smooth and rough surfaces, as suggested in Figure 1. During the electrospinning process, PVP fibers were directly electrospun onto the substrates for 30 min.

2.2. Characterization. The morphology of the as-spun fibers and substrates were examined by using a scanning electron microscope (SEM, Phenom ProX, Phenom Scientific Instruments Co., Ltd.) at 10 kV, and all samples were coated with gold layer for 30 s before analysis. The electrostatic attenuations of the as-spun meshes on different substrates were examined by using a static decay analyzer (Electrico-Tech Systems Inc. Glenside, PA). The adhesion force was measured by using a home-made pulling system, as shown in Figure 2. The width of the kraft paper strip (d_2) and pulling height (h_1) were measured by using a ruler and were fixed at 1 cm and 5 cm. The width of the electrospun fibers leaving the substrates was also measured by using a ruler. The thickness of the electrospun meshes h_2 was measured by using a film thickness gauge. The pulling force F was provided and measured by the weight of poises. With these data, the adhesion force can be calculated by the following equation:

$$f_a = \frac{\left[F - k\left(\sqrt{a^2 + b^2} - b\right)\right] h_2}{2bc}, \qquad (1)$$

where $a = h_1 - h_2$, $2b = d_1 - d_2$, and k is the elastic modulus of the fibrous meshes. By analyzing the adhesion force, we can understand the mechanism of the adhesion between electrospun fibers and substrates and then apply it to the actual applications.

3. Results and Discussion

Firstly, we examined the morphologies of the electrospun PVP fibers on different substrates under different electrospinning parameters. As can be found in Figure 3, the diameters of the PVP fibers show obviously changes onto different substrates that the average diameter of as-spun fibers onto conductive aluminium foil was smallest, was medium on wood pulp paper, and was largest on the silicon paper. The different fiber diameters might result from the conductivity of the substrates. Moreover, the

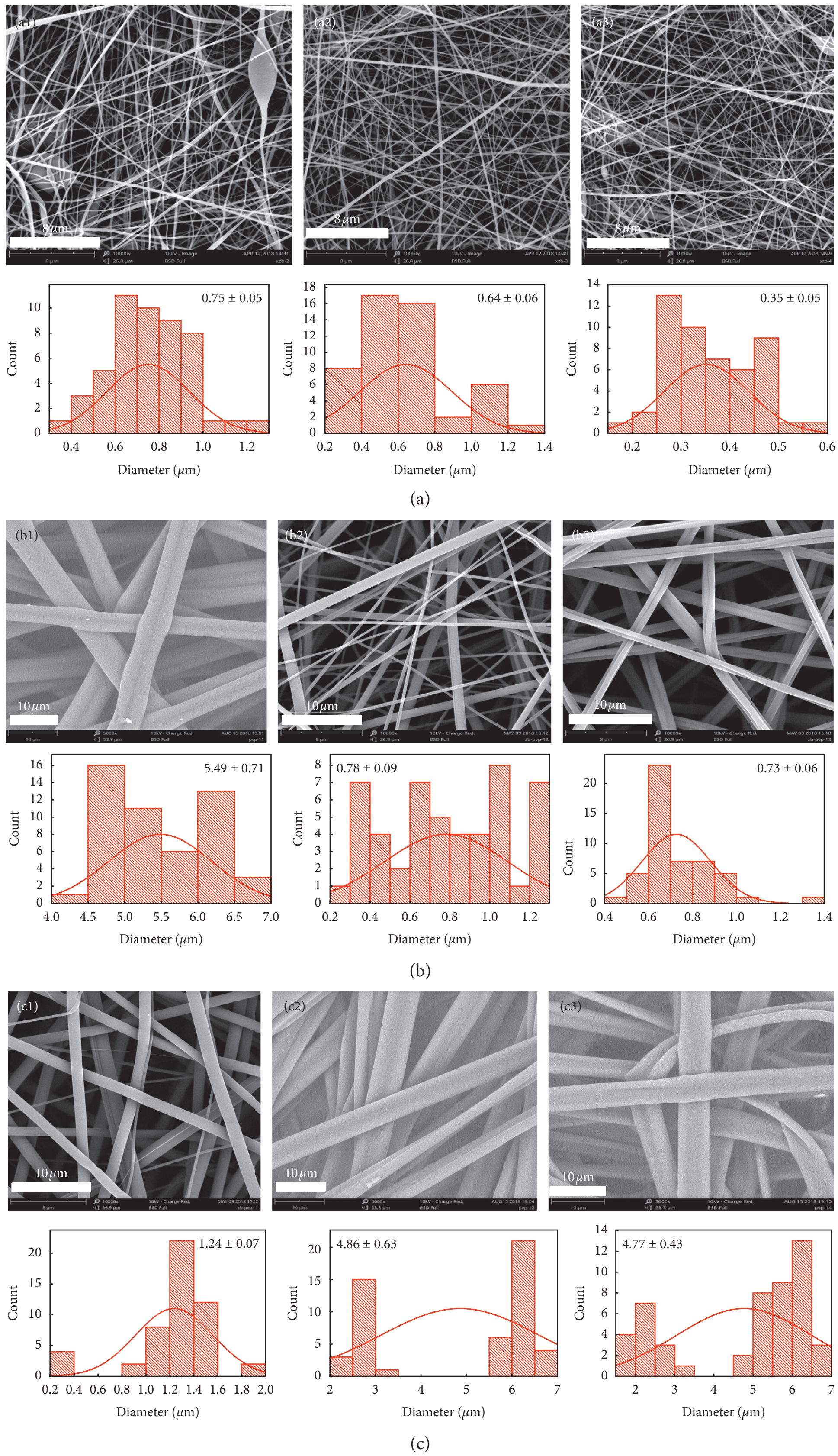


FIGURE 3: SEM images of electrospun PVP fibers onto different substrates: (a) aluminium foil, (b) wood pulp paper, and (c) silicon paper at different electrospinning voltages of 11 kV (a1, b1, c1), 12 kV (a2, b2, c2), and 13 kV (a3, b3, c3). The inset images showed the average diameters of the as-spun fibers and their distributions.

Table 1: Experimental data collected from measurement of the adhesion force f_a by using the home-made pulling system.

Substrates	Voltage (kV)	h_1 (cm)	$\overline{h_2}$ (mm)	d_1 (cm)	d_2 (cm)	$\overline{F}$ (N)	c (mm)	k	$\overline{f_a}$ (N/cm^{-2})
Aluminium foil	11	0.5	0.047	2.8	0.5	0.2298	15	0.4438	0.185166
	12	0.5	0.035	1.5	0.5	0.2895	15	0.4438	0.196429
	13	0.5	0.044	1.0	0.5	0.3021	15	0.4438	0.235372
Virgin pulp paper	11	0.5	0.062	2.0	1.0	0.8706	15	0.4438	0.014186
	12	0.5	0.040	3.0	1.0	0.5754	15	0.4438	0.030572
	13	0.5	0.062	4.4	1.0	0.4038	15	0.4438	0.030773
Silicon paper	11	0.5	0.096	5.4	1.0	0.0683	15	0.4438	0.007558
	12	0.5	0.093	4.4	1.0	0.1579	15	0.4438	0.008561
	13	0.5	0.091	3.9	1.0	0.0614	15	0.4438	0.013341

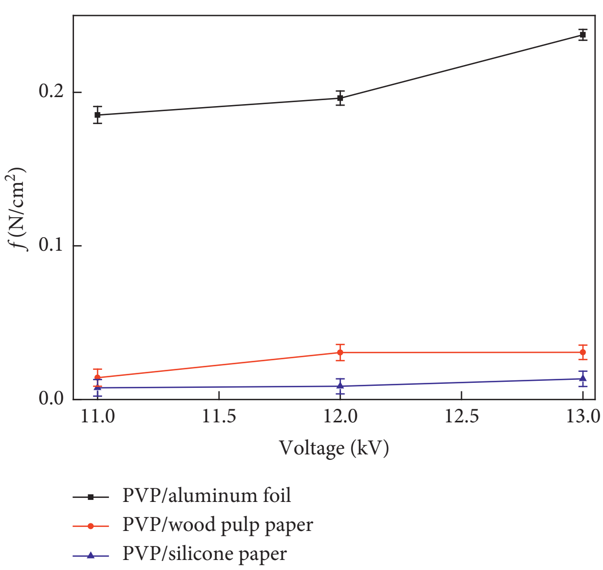


Figure 4: Plots of the adhesion force f_a on different substrates varied with increasing spinning voltage.

increase of electrospinning voltage also resulted in thinner fiber diameters as suggested in Figure 3. The adhesion force may be different consequently due to the different number of fibers deposited per unit area. It was indicated that the increase in packing density increases would involve the increased surface contact between the electrospun fibers and substrate surfaces and then allow stronger van de Waal forces to act [16]. As can be observed that there are more fibers on the same area, a larger adhesion force may be achieved.

By using the home-made pulling system shown in Figure 1, we collected all the related data and calculated the adhesion force accordingly. As shown in Table 1 and Figure 4, one can obviously find that the adhesion force of the electrospun PVP fibrous meshes is larger as spinning voltages increased on all the substrates, which may not only ascribe to the thinner fiber diameter but also result from the higher electrostatic adherence effect. Moreover, the adhesion force on the conductive aluminium foil is much higher than the insulated papers due to the thinner fiber diameters. Furthermore, the adhesion force on the rough wood pulp paper is found to be stronger than in the smooth silicon paper. Apart from the effect of fiber diameter, there was also an effect of the roughness of the substrates. It has been indicated that with more surface asperities, greater mechanical interlocking between the fibers and the substrate surface can be expected and hence greater adhesion [13].

With the increase of spinning voltage, the diameter of fibers on different substrates will change. The change of fiber diameter will cause the change of fiber adhesion. As shown in Figure 5, as the spinning voltage increases, the diameter of the fiber will become smaller and the adhesion of the fiber will increase.

To further understand the mechanism of the adhesion force on different substrates, we examined the electrostatic decay of PVP fibers on different substrates, as suggested in Figure 6. It is shown that for electrospun fibers on the conductive aluminium foil, the given electrostatic voltage decayed quickly, which may help the charged electrospun fibers adhere to the aluminium foil fast as soon as they contacted the aluminium foil during electrospinning process. The insulated papers showed a slow decay trend and the silicon paper was the slowest, which corresponds to the adhesion force tested results as suggested in Figure 4 and Table 1.

When the substrate is aluminum foil, the adhesion test results are in the correct range by comparing with the test results of other methods. We have compared different measurement adhesion methods, and the specific results are shown in Table 2. The test results are in a reasonable range. This method is proved to be reliable. The adhesion of different substrates is tested by this method.

In order to verify the applicability of this method, the adhesion of different fibers on aluminium foil was measured by this method. PAN and TPU were spun on aluminium foil to measure the adhesion test results, as shown in Table 3 and Figure 7.

It can be seen from the conclusions in Table 3 and Figure 7 that this method is applicable to test adhesion not only on PVP fibers but also on other fibers.

4. Conclusion

In summary, we reported a new method to measure the adhesion force between *in situ* electrospun meshes and substrates by direct pulling. Several substrates were selected including smooth conductive aluminium foil, rough insulated wood pulp paper, and smooth insulated silicon paper.

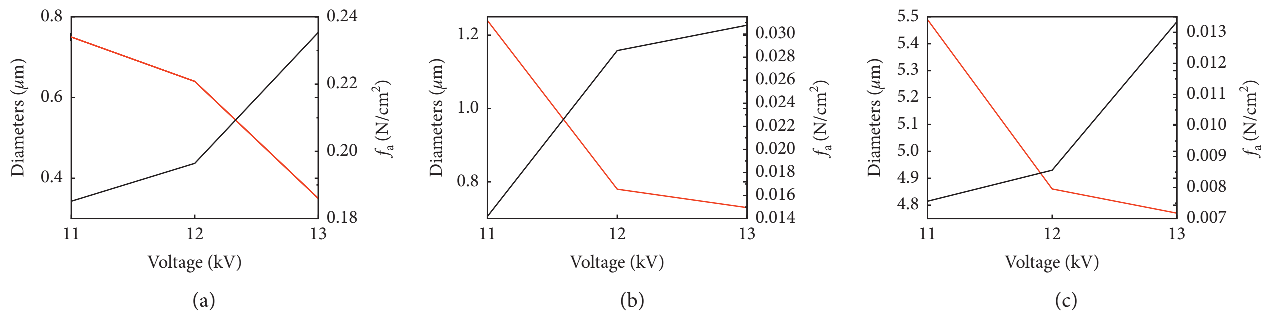


FIGURE 5: As the spinning voltage increases, adhesion and fiber diameter change. (a) The change of PVP fiber on aluminium foil. (b) The change of PVP fiber on wood pulp paper. (c) The change of PVP fiber on silicone paper.

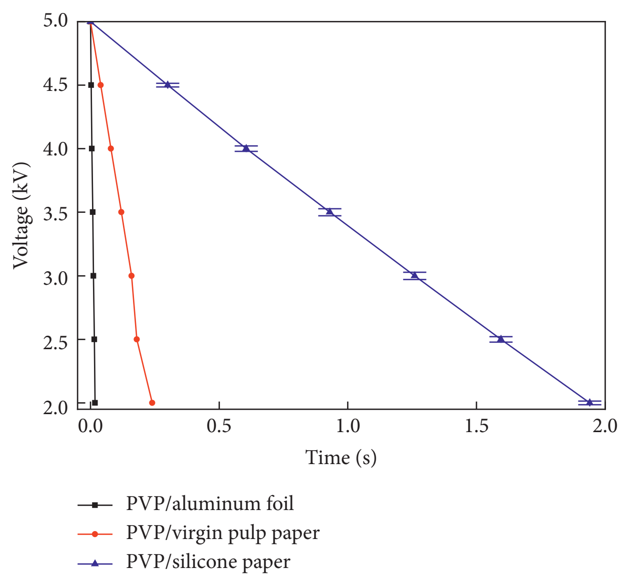


FIGURE 6: Electrostatic decay of the electrospun fibers on different substrates.

TABLE 2: Comparison of different methods.

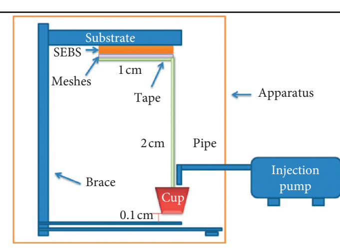
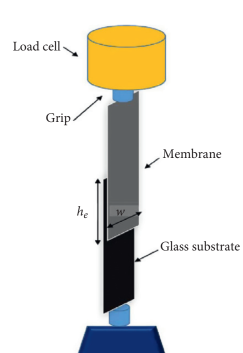
Method	Experimental materials	Test equipment chart	Experimental result adhesion (mN)	Merit and demerit
Quantitatively measure the adhesion with a weight method	PEO		68~220	(1) Large test error (2) Complex sample making
AFM adhesion measurements	PVDF		165	(1) Operation complex (2) Exercise equipment expensive

Table 2: Continued.

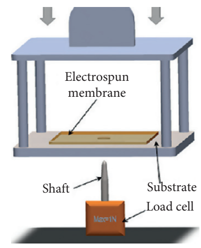
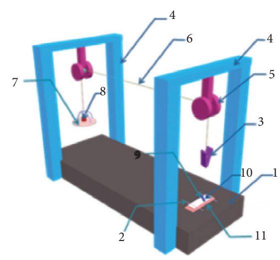
Method	Experimental materials	Test equipment chart	Experimental result adhesion (mN)	Merit and demerit
Shaft loaded blaster test (SLBT)	PVDF		206 ± 26	(1) Computational complexity (2) Complex sample making
A direct pulling method to measure the adhesion	PVP		185~215	(1) Simple and intuitive use (2) Equipment is cheap (3) Simple sample making

Table 3: Adhesion of different fibers.

Fiber	Voltage (kV)	h_1 (mm)	h_2 (cm)	d_1 (cm)	d_2 (cm)	F (N)	c (mm)	K	f_a (N/cm^2)
PAN	11	0.021	0.5	3.6	1.0	0.1931	15	0.0495	0.042552
	12	0.015	0.5	4.2	1.0	0.3181	15	0.0495	0.065753
	13	0.022	0.5	3.2	1.0	0.3273	15	0.0495	0.093455
	14	0.035	0.5	2.6	1.0	0.3598	15	0.0495	0.135811
TPU	11	0.031	0.5	2.9	1.0	0.3191	15	0.0072	0.122492
	12	0.022	0.5	3.1	1.0	0.5684	15	0.0072	0.200121
	13	0.034	0.5	2.0	1.0	0.4216	15	0.0072	0.305152
	14	0.060	0.5	2.8	1.0	0.7785	15	0.0072	0.320577

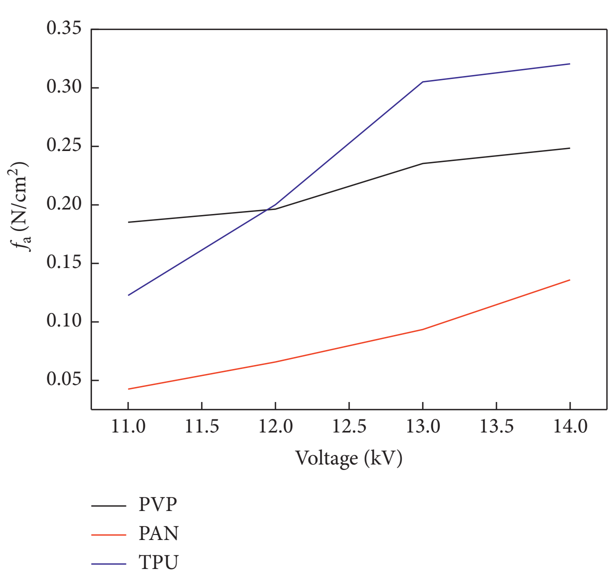


Figure 7: With the increase of spinning voltage, the adhesion of different fibers on aluminium foil changes.

PVP nanofibers were electrospun into fibers onto these substrates under different voltages. The examined adhesion force suggested that conductive substrates and increasing voltage may help to increase the adhesion force due to the thinner fiber diameter and improved electrostatic force. It was also found that the roughness of the substrates may increase the adhesion force. Moreover, these results also indicated that the new method to measure the adhesion force is effective.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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(ZR2017BA013), and the China Postdoctoral Science Foundation (2017M612200).

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