Preparation and Oil Filtration Properties of Electrospun Nanofiber Composite Material

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ABSTRACT

In this paper, PVA electrospun nanofiber was prepared on the surface of three different automobile engine oil filtration materials including polyester nonwoven, glass fiber nonwoven, and cotton pulp filtration paper. It was found that the substrate of cotton pulp filtration paper and the nanofiber layer had better adhesive effect. Then we A comparison of fiber diameter, pore diameter, filtration accuracy and pressure drop between the cotton pulp paper and nanofiber composite filtration material was then made. The results show that the nanofiber composite material had smaller pore diameter and filtration accuracy, higher pressure drop, and better oil filtration property. Additionally, the difference of pressure drop between the substrate and nanofiber composite material increased with increasing flow rate of experimental oil. The goal of this paper was use the electrospun nanofiber in the automobile engine oil filtration.

Keywords: Automobile, Electrospinning, Nanofiber, Oil filtration

INTRODUCTION

Porous automobile engine oil filtration material [1], including different cotton pulp filter paper [2], polyester nonwoven, and glass fiber nonwoven is used to separate different particles from fluids. With the development of the automobile industry, the usage of automobile engine oil filtration materials is also increasing in China. However, the commonly used oil filtration materials have some defects in application, for instance, higher pore diameter and pressure, and lower filtration efficiency.

In order to improve these shortcomings of commonly used automobile engine oil filtration materials, one of the frequently-used methods is electrospinning technology. Donaldson [2-3] is has a mature technique to produce electrospun nanofiber and composite filtration materials. After a review of literatures on filtration materials, we found that the electrospun nanofiber was mostly applied in air filtration [4] and seldom used in automobile engine oil filtration. In practical application of automobile engine oil filtration, some oil filtration materials have a two-layer, three-layer or multi-layer structure [5-6]. As to the automobile engine oil filter, the filtration materials should be folded to form a lamellar structure and be adhered to the automobile filter cartridge.

Up to this point the electrospinning technology has been used to prepare nanofiber from a few nanometers to hundreds of nanometers. The principle [7-8] of this technique is that a solution of polymer can be sprayed to form a jet in a high voltage electrostatic field [7] and collected by a special device of substrate. The nanofiber is a superfine fiber [9] which has some special properties which can be applied in many respects [10], for instance, tissue engineering scaffold, biological dressing, nano electronic devices, battery and electrode material, chemical and biological sensors, protective clothing, environmental cleaning materials, and filtration [11]. A number of polymers [12] can be electrospun to form nanofibers, for instance, PCL, PVA, PU, PAN, PGA, PLA, PC, PS, some polymer blends, and polymer/inorganic hybrids [10]. Among them, PVA [13-14] has good chemical stability, thermal stability, solubility and special viscosity which is water soluble polymer at at temperatures of 80-90℃.

In order to expand the application of electrospun nanofibers and discuss automobile engine oil filtration properties, we prepared PVA nanofibers which were formed on the surface of different substrates including polyester nonwoven, glass fiber nonwoven, and cotton pulp filtration paper. The experimental results showed that the cotton pulp filtration paper and the nanofiber layer had a better adhesive effect. Then we made a comparison of automobile engine oil filtration properties between the cotton pulp filtration paper and nanofiber composite material.

EXPERIMENTAL

Material of Substrates

In order to research the oil filtration property of substrate and nanofiber composite material, we selected three different kinds of automobile engine oil filtration materials from the market. These substrates included polyester nonwoven, glass fiber nonwoven, and cotton pulp filtration paper which were purchased from HeNan Xin Xiang Chang Cheng Filtration material Company Limited of China. The substrates had the same nominal filtration accuracy in practical application and are the commonly used automobile engine oil filtration materials.

Property Measurement of Substrates

The weight (mass/unit area) was measured with an AR 2140 Electron Balance. Thickness was measured with an YG 141N device in accordance with standard of GB/T 3820-1997. Air permeability was measured with an YG 461E device in accordance with the standard of GB 5453-85. Mechanics properties were measured with an YG 065 device in accordance with the standard of GB/T 3923-1997.

PVA Material

The experimental PVA polymer, $(C_2H_4O)_n$ and n=124, was purchased from XiLong Chemical Company Limited. Before the electrospinning process, the PVA was dissolved in a water bath of 80℃ and made into a solution at a concentration of 7%. The experimental temperature was the standard room temperature and the relative humidity was 65%.

Electrospinning Setup and Process

The electrospinning device including the high voltage power supply, injection needle, collector roll and some fixed installations is shown in *Figure 1*. The high voltage power supply was settled by fixed equipment 1. The fixed unit 2 was mainly used to control the needle position and adjust the collector distance between sample and needle. The fixed unit 3 was used to support the weight of the rotating roll and adjust collector distance. Before electrospinning nanofiber, the PVA solution was sucked into the needle which was fastened by fixed unit 2. Additionally, the substrate was fixed in the collector roll which rotated at a certain rate as low as possible to get a uniform nanofiber layer. The filament was presented at a relatively chaotic state and could not be collected by the rotating roll at a lower value of voltage power supply before experimentation. After a continuously adjusting process of voltage and collection distance, we found that the PVA nanofiber could be collected well on the surface of substrates.

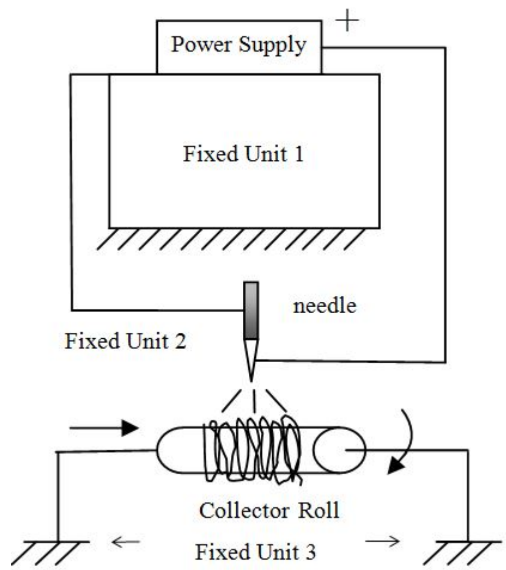

FIGURE 1. Schematic diagram of electrospinning set-up and process.

Experimental Setup of Filtration Property Measurement

The pore diameter and filtration accuracy were measured with an MP-15K β_x instrument in accordance with the standard of GB 5249-85 permeable sintered metal materials and determination of bubble test pore size (see *Figure 2*). The pore diameter was calculated by the following equation:

$$d_p = \frac{4\gamma \cos\theta}{\Delta P} \quad (1)$$

where d_m is effective pore diameter, μm . γ is the surface tension of isopropyl alcohol, N/m. ΔP is the static pressure drop produced on the surface of porous material, Pa. θ is the contact angle between isopropyl alcohol and porous material.Where $\theta = 0°, \cos\theta = 1$ and $d_p = 4\gamma / \Delta P$.

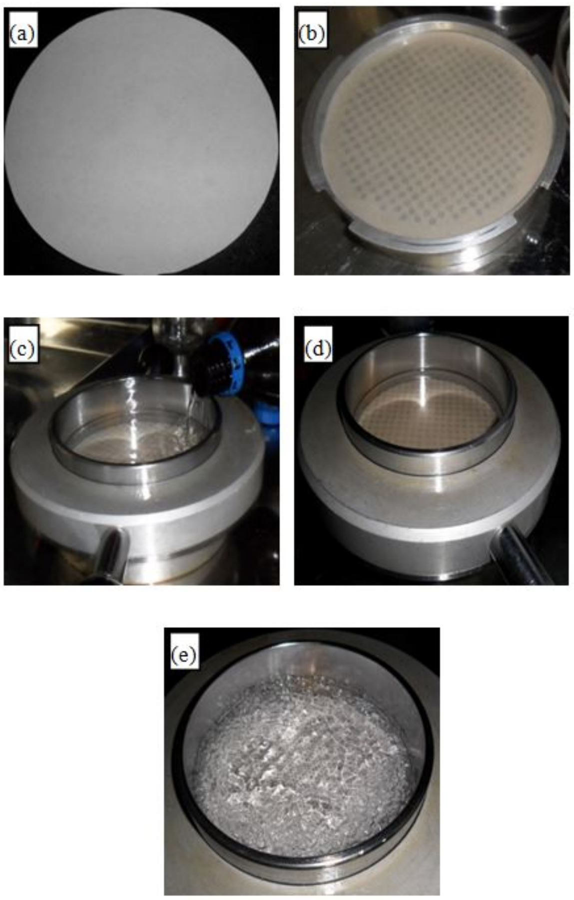

FIGURE 2. The experimental setup and process of pore diameter measurement. (a) the samples were cut into a circular area of 100 cm^2,(b) the sample was put into the vessels, (c) the isopropyl alcohol was poured into vessels, (d) no bubbles appeared in the surface of sample and (e) the bubbles appeared in the surface of sample.

Figure 3 shows the LCS-6 experimental setup for measuring the pressure drop in accordance with ISO 3968:2001Hydraulic Fluid Power-Filters-Evaluation of Differential Pressure Versus Flow Characteristics.

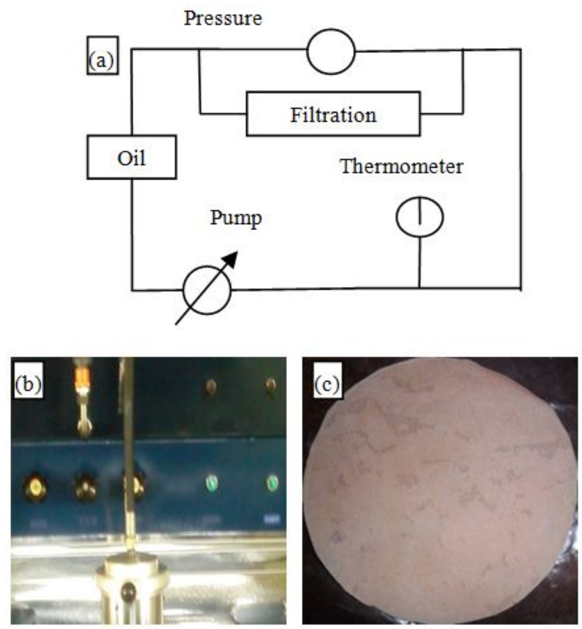

FIGURE 3. Experimental setup of pressure drop measurement. (a) the principle of experimental setup,(b) main system of actual experimental setup,(c) sample after oil filtration experiment.

The experimental oil first flowed through the experimental fixture and then flowed through the experimental fixture containing the filtration material. The pressure drop produced on both sides of material was defined as

$$\triangle p = Q_1 - Q_0 \qquad (2)$$

where Δp is pressure drop of material, KPa. Q_1 is the total pressure of material and experimental fixture, KPa. Q_0 is the pressure of experimental fixture, KPa.

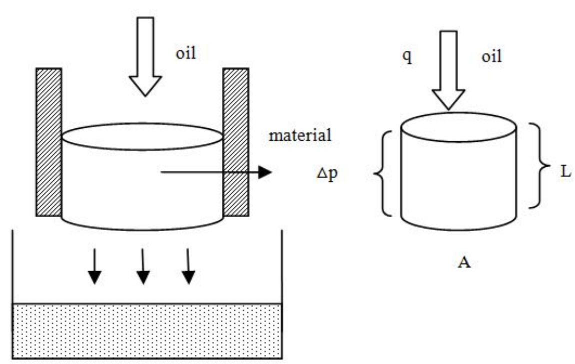

FIGURE 4. Modeling of oil filtration process.

Theoretical Analysis of Oil Filtration

As we know that the obvious pressure drop could be produced on both sides of filtration material as the experimental liquid getting through the porous material in accordance with Darcy’s Law [15]. In order to unify the meaning of the same parameters, we adopted part of different alphabetic symbols to express the same significance [16-17]. So the pressure drop [16] could be expressed by

$$\Delta p = 16\frac{k_1 L \mu q}{g_c d_p^2 \varepsilon} \tag{3}$$

where q is flow rate, m/s. μ is viscosity of experimental liquid, Pa·s. L is thickness of porous material, mm. d_p is pore diameter, μm . ε is porosity,%. g_c is the acceleration of gravity, m/s^2. Δp is pressure drop on both sides of the material, KPa. k_1 is coefficient.

The relation between flow rate and flux of liquid [17-18] can be expressed by

$$q = \frac{Q}{At} \tag{4}$$

Where Q is flux, L/min. A is area of material, cm^2. t is experimental time, min.

RESULTS AND DISCUSSION

Comparison of Substrate Properties

Table I shows the properties of polyester nonwoven, glass fiber nonwoven, and cotton pulp filtration paper. Through comparison of filtration properties among these three filtration materials, we found that polyester nonwoven and glass nonwoven had the better filtration effect, while the cotton pulp filtration paper had the worst filtration effect.

The SEM Figures of Samples

The electrospinning nanofiber was formed on the different surface of substrates including polyester nonwoven, glass fiber nonwoven and cotton pulp filtration paper, which are shown in *Figure 5* separately.

TABLE I. Experimental result of ten different filtration materials.

	Polyester Nonwoven	Glass Fiber Nonwoven	Cotton Pulp Paper
nominal filtration accuracy/ μm	10	10	10
thickness/mm	3.895	0.61	0.718
weight/g·m^{-2}	257.12	76.14	194.31
mean pore diameter/ μm	44.7	23.6	39.2
maximum of pore diameter/ μm	44.9	26.8	39.3
actual filtration accuracy / μm	9.1	5.2	15
maximum fiber diameter/ μm	19.2	5.6	31.1
minimum fiber diameter/ μm	0.2	1.5	9.1
mean fiber diameter/ μm	10.67	3.42	23.85
porosity/%	95.22	95.07	77.45
air permeability/mm·s^{-1}	432.498	333.146	59.397
breaking strength/N	571.1	22.419	357.78
breaking elongation/mm	27.701	2.565	4.955
ratio of elongation/%	13.85	1.282	2.477
breaking work/J	54.314	54.26	55.17
breaking time/s	16.621	1.539	2.973
bursting strength/N	1001.1	12.6	82.539
bursting elongation/mm	34.785	19.367	21.633

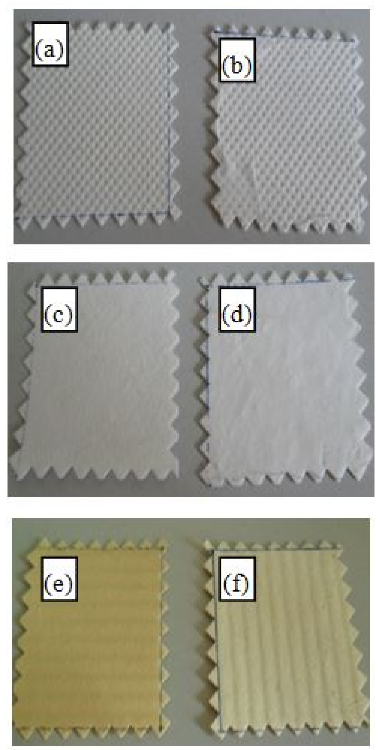

FIGURE 5. The substrate and electrospinning nanofiber composite filtration material.(a) polyester nonwoven,(b) polyester nonwoven nanofiber composite material,(c) glass fiber nonwoven,(d) glass fiber nonwoven nanofiber composite material,(e) cotton pulp paper and (f) cotton pulp paper nanofiber composite material.

The high voltage was 27.85KV, concentration of PVA was 7%, flow rate of syringe needle was 1.9 mL/h and the collect distance was 10cm. The SEM figures of substrates and nanofiber composite materials are shown in *Figure 6*. Compared with the disorderly distribution of fibers on the surface of polyester nonwoven (see *Figure 6* (a) and (b)), it can be seen that some nanofibers are bonded together which has a bifurcate structure on the surface of polyester nonwoven (see *Figure 6* (c) and (d)). Moreover, the beads are also formed in the naonfiber. *Figure 6* (e) and (f) are the glass fiber nonwoven, and (g) and (h) are the nanofiber composite material. It can be seen that the nanofibers are in a good state on the substrate of glass fiber nonwoven. However, the nanofiber layer can be easily separated from the substrate of glass fiber nonwoven due to the poor bonding effect (see *Figure 6* (i) and (j)). (k) is the substrate of cotton pulp filtration paper and (l) to (m) are the nanofiber composite material. Compared with the glass fiber nonwoven nanofiber composite material and polyester nonwoven nanofiber composite material, the cotton pulp paper nanofiber composite material has a better bonding effect between the substrate and nanofibers. So we use the cotton pulp filtration paper and its nanofiber composite material to make a deep comparison of the filtration property.

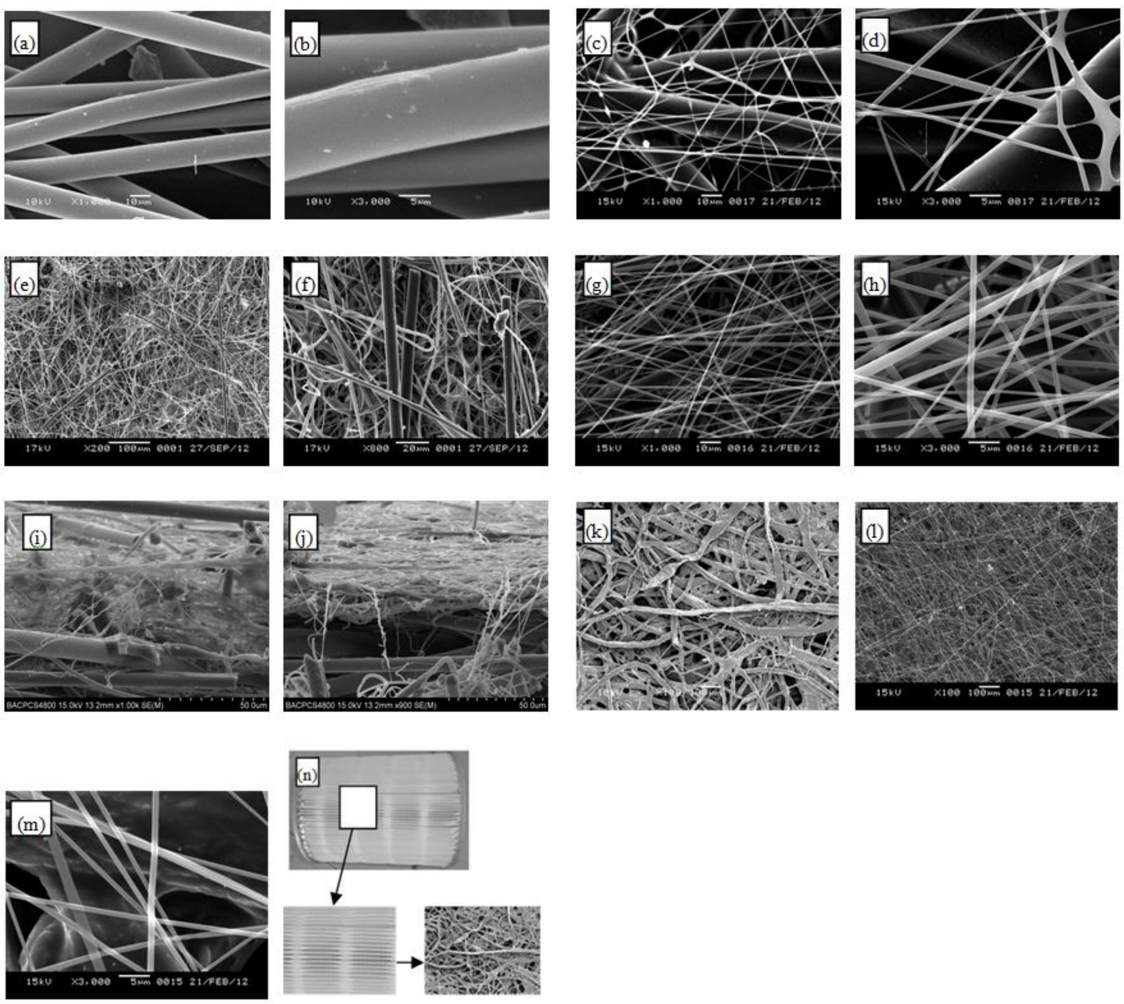

FIGURE 6. SEM figures of substrate and electrospinning nanofiber composite filtration material. (a) and (b) are the polyester nonwovens, (c) and (d) are the nanofibers formed on the surface of polyester nonwoven. (e) and (f) are glass fiber nonwovens, (g) and (h) are the nanofibers formed on the surface of glass fiber nonwoven, (i) and (j) are the two layers between glass fiber nonwoven and nanofiber. (k) is cotton pulp filtration paper, (l) to (m) are the nanofibers formed on the surface of cotton pulp filtration paper. The electrospinning time of (c) and (d), (l) to (m) were 3 hours, while the (g) to (j) was 4 hours. (a),(b) and (k) were observed by JSM-6360LV Scanning Electron Microscope, (i) and (j) were observed by JSM-6360LV Scanning Electron Microscope, other figures were observed by JSM-5610 Scanning Electron Microscope. (n) is an actual automobile engine oil filter (the filter is provided by a Filter Company and the filtration material is cotton pulp paper).

Comparison of Fiber Diameter

On the basis of circular shape of fiber diameter, the calculation of average, standard deviation and coefficient variation of fiber diameter are as follows (the number of Eq. (6) is 19 and N=20) [19].

$$\bar{x} = \frac{1}{20}\sum_{i=1}^{20} x_i \quad (5)$$

$$s = \sqrt{\frac{1}{19}\sum_{i=1}^{20}(x_i - \bar{x})^2} \quad (6)$$

$$CV = \frac{s}{\bar{x}} \times 100\% \quad (7)$$

where i is fiber number, x_i is fiber diameter, $\bar{x}$ is mean value, s is standard deviation and CV is coefficient variation.

The results of fiber diameter of cotton pulp paper and electrospinning nanofiber are calculated by Eq. (5) to Eq. (7), and the values are shown in *Table II*.

TABLE II. Experimental results of fiber diameter.

	Fiber Diameter Of Cotton Pulp Paper / Nm	Fiber Diameter Of Electrospinning Pva Nanofiber /Nm
maximum	31100	1707.01
minimum	9100	523.93
mean value	23850	956.05
standard deviation	7800	312.61
coefficient of variation (%)	32.70	32.69

It can be seen that the mean value of fiber diameter of substrate and electrospinning nanofiber are 23850 nm and 956.05 nm, the coefficient variation of them are 32.7% and 32.69%, respectively. Compared with the fiber diameter of cotton pulp filtration paper, the electrospinning nanofiber can greatly decrease the fiber diameter in a nano scale. The fiber diameter distribution frequencies of substrate and electrospinning nanofiber are shown in *Figure 7*. The results show that the fiber diameter of substrate distributed in the interval of 10.2-13.3 μm is 25% and the electrospinning nanofiber distributed in the range of 760-878.5 nm and 878.5-997 nm are 25%。

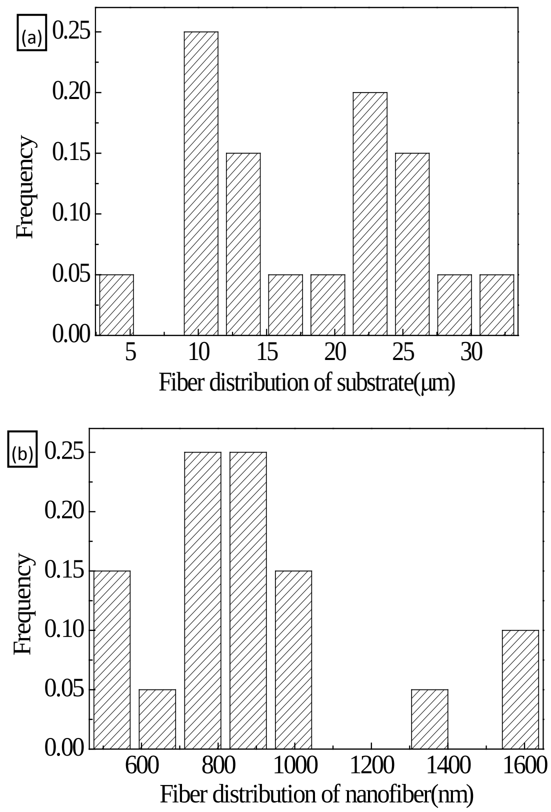

FIGURE 7. The distribution frequency of fiber diameter. (a) substrate of cotton pulp paper and (b) electrospinning nanofiber.

Comparison of Pore Diameter

Besides fiber diameter, the pore diameter of filtration material is another important parameter which can be measured by the MP-15K β_x instrument. *Table III* shows the results of pore diameter of the substrate and electrospinning nanofiber composite material. The mean value and maximum of pore diameter of substrate are 39.2 μm and 39.3 μm, while the two values of nanofiber composite material are 37.6 μm and 38.3 μm respectively. Through a comparison of pore diameter with substrate, it can be found that the nanofiber composite material has the smaller pore diameter.

TABLE III. Experimental results of pore diameter.

Sample	Pressure of First Bubble /Pa	Pressure of Group Bubbles /Pa	Average of Pore Diameter / μm	Maximum of Pore Diameter / μm
substrate	2166	2170	39.2	39.3
composite material	2315	2360	37.6	38.3

Comparison of Filtration Accuracy

The filtration accuracy of substrate and electrospinning nanofiber composite material is 15.0 μm and 14.4 μm, respectively. And the results show that the nanofiber composite material has the better filtration effect. Theoretical analysis the change of filtration accuracy is shown in *Figure 8*. The results show that some smaller particles leaking from the substrate can be easily intercepted by the nanofiber layer.

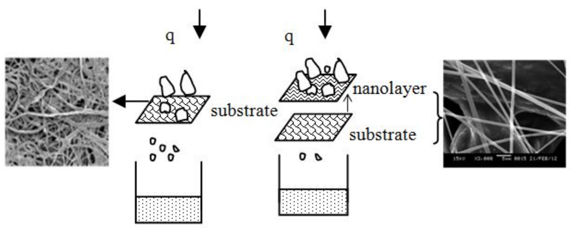

FIGURE 8. Change of filtration accuracy. The top layer is nanofiber and the substrate is cotton pulp filtration paper.

Comparison of Pressure Drop

Another important parameter is pressure drop which was measured by LCS-6 Pressure Drop–Flow Device at Henan Xinxiang TianYi Filter Technology Co Ltd. of China. *Table IV* shows the value of pressure drop calculated from Eq. (2).

TABLE IV. Experimental results of pressure drop.

		flow rate/(L/min)			
		1	2	3	4
pressure drop of substrate/KPa	Q_1	67	81	96	114
	Q_0	63	76	91	107
pressure drop of nanofiber	Q_1	68	89	111	135
composite material/KPa	Q_0	63	76	91	107

Figure 9 is the result of pressure drop comparison between the substrate and nanofiber composite material. It can be seen that the nanofiber composite material has the higher pressure drop on both sides of filtration material due to the smaller pore diameter. Moreover, the difference of pressure drop between the substrate and nanofiber composite material increases as the flow rate of experimental oil increasing from 1 L/min to 4 L/min.

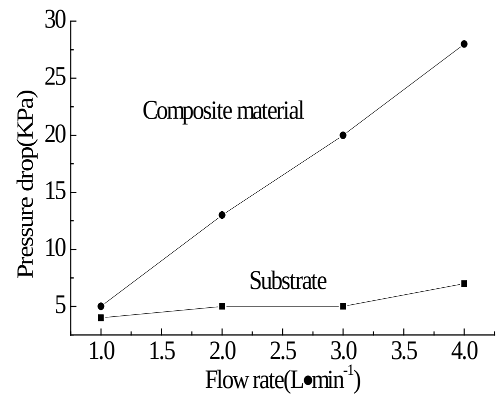

FIGURE 9. Pressure drop comparison between substrate and nanofiber composite material.

From Eq. (3) we know that the relation between pressure drop and pore diameter is $\Delta p \propto 1/d_p^2$, and the relation between pressure drop and flow rate is $\Delta p \propto q$. So the pressure drop on both sides of filtration material increases as the decreasing of pore diameter and the increasing of flow rate. The change of pressure drop of nanofiber composite material is in agreement with the previous research. However, this is a contradictory aspect among pore diameter, pressure drop and filtration accuracy. The smaller pore diameter of nanofiber composite material means a better filtration effect; on the contrary, the smaller pore diameter can produce a higher pressure drop on both sides of nanofiber composite material.

CONCLUSION

The PVA nanofiber was formed on the surface of three different substrates including polyester nonwoven, glass fiber nonwoven, and cotton pulp filtration paper at the constant condition of high voltage, concentration of PVA, flow rate of PVA solution, and collect distance. The experimental results showed that the cotton pulp filtration paper and the nanofiber layer had a good adhesive effect. Then we made a deep comparison of fiber diameter, pore diameter, filtration accuracy, and pressure drop between the cotton pulp filtration paper and nanofiber composite filtration material.

Compared with the cotton pulp filtration paper, the nanofiber had the smaller fiber diameter of 956.05 nm, and the nanofiber composite material had the smaller mean pore diameter of 37.6 μm. Moreover, the nanofiber composite material had the smaller filtration accuracy of 14.4 μm.The higher pressure drop produced on the nanofiber composite filtration material as the experimental oil flowing through the material. Moreover, the difference of pressure drop between the substrate and nanofiber composite material increased as the flow rate of experimental oil increasing from 1 L/min to 4 L/min.

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REFERENCES

[1] Rubenstein D.I., Koehl M.A.R. The mechanisms of filter feeding some theoretical considerations, The American Naturalist, 111(1977)981.

[2] Grafe T., Gogins M., Barris M., Schaefer J,, Canepa R., Nanofibers in filtration applications in transportation. Presented at filtration 2001 international conference and exposition of the INDA (Association of the Nonwovens Fabric Industry).Chicago. Illinois, 2001.

[3] Graham K., Ouyang M., Raether T., Grafe T., McDonald B., Knauf P.,Polymeric Nanofibers in air filtration applications, The fifteenth annual technical conference & Expo of the American filtration & separations society, Galveston, Texas, 2002.

[4] Qin X.H., Wang S.Y., Filtration properties of electrospinning nanofibers, J of Applied Polymer Science, 102 (2006)1285.

[5] Feng J.Y., Zhang J.C., Zhang H., Yang D.X., Study on the structure and performance of the multi-layer filter materials of automobile oil filter cartridge, Advanced Materials Research, 396-398 (2012)1545.

[6] Feng J.Y., Zhang J.C., Zhang H., Yang D.X., Study on the relationship between nominal filtration accuracy and absolute filtration accuracy of the automobile engine oil filter materials, Advanced Materials Research, 476-478 (2012)2213.

[7] Hohman M.M., Shin M., Rutledge G., Brenner M.P., Electrospinning and electrically forced jets Stability theory, Physics of Fluids, 13 (2001) 2201.

[8] Huang Z.M., Zhang Y.Z., Kotaki M., Ramakrishna S., A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites Science and Technology, 63 (2003) 2223.

[9] Wang H.S., Fu G.D., Li X.S., Functional polymer nanofibers from Electrospinning, Recent Patents on Nanotechnology, 3 (2009) 21.

[10] Kumbar S.G., Nukavarapu S.P., James R., Hogan M.V., Laurencin C.T., Recent patents on electrospun biomedical nanostructures: an overview, Recent patents on biomedical engineering, 1 (2008) 68.

[11] Shaffer R.E., Rengasamy S., Respiratory protection against airborne nanoparticles: a review, J. Nanopart Res, 11 (2009)1661.

[12] Frenot A., Chronakis I.S., Polymer nanofibers assembled by electrospinning, Current Opinion in Colloid and Interface Science, 8, (2003)64.

[13] Chuangchote S., Supaphol P., Fabrication of Aligned Poly (vinyl alcohol) Nanofibers by Electrospinning, J. Nanosci. Nanotechnol, 6 (2006) 125.

[14] Peresin M.S., Habibi Y., Zoppe J.O., Pawlak J.J., Rojas O.J., Nanofiber Composites of Polyvinyl Alcohol and Cellulose Nanocrystals: Manufacture and Characterization, Biomacromolecules, 11 (2010) 674.

[15] Yoon K., Kim K., Wang X.F., Fang D.F., Hsiao B.S., Chu B., High flux ultrafitration membranes based on electrospun nanofibers PAN scaffolds and chitosan coating, Polymer, 47, 2434(2006).

[16] Yim S.S., Kwon Y.D., Kim H., Effects of pore size, suspension concentration, and pre-sedimentation on the measurement of filter medium resistance in cake filtration, Korean J. Chem. Eng., 18 (2001)741.

[17] Zhang S., Shim W.S., Kim J., Design of ultra-fine nonwovens via electrospinning of Nylon 6: Spinning parameters and filtration efficiency, Materials and Design, 30 (2009) 3659.

[18] Podgorski A., Balazy A., Gradon L., Application of nanofibers to improve the filtration efficiency of the most penetration aerosol particles in fibrous filters, Chemical Engineering Science, 61, 6804(2006).
[19] Al-Saleh M.F., A.E., Properties of the Standard Deviation that are Rarely Mentioned in Classrooms, Austrian J of Statistics, 38, 193(2009).

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