Preparing and Testing of Nanometer Polymeric Filters (Polyethylene oxide, Polyurethane) Manufactured by Electrospinning and Determining Their Properties

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ABSTRACT: *The aim of this research is to manufacture and test nanofiber filters made of Polyurethane (PU) and Polyethylene oxide (PEO) using electrospinning. In addition, the principle of electrospinning process explained. The effect of polymer percentage, electric voltage and the distance between the needle and the collector were studied. Filter fiber diameter was measured on the Scanning Electron Microscope (SEM) and reached to about 100 nm for PU and about 40 nm for PEO. The filters had been tested by placing the E. coli bacteria on their surface and the test showed that they did not penetrate through the filter therefore the fibers produced can be used to manufacture filters with high filtration accuracy.*

Keyword*: Electrospinning, polyurethane, Polyethylene oxide, Nanofibers, Filters*

1. Introduction

Manufacturing technology shifted from micron to nano, where nanoscience expanded rapidly and led to the creation of fewer fibers than micron. But the main problem with this technology is that the raw materials used are limited and must be of high elasticity and viscosity to ensure their cohesion during elongation, where the force of electrospinning on the polymer nozzle is used to extrude fiber to the collector [1,2,3].

Happel (1959) studied the effectiveness of the filter through the manufacture of single fibers. Stechkin (1965), Liu (1982) and Brown (1998) studying of filters with one-dimensional fibers [4]. Studying the effect of single and combined fibers for filter by the filter with two-dimensional fibers 2D by Kirsh (2003) [5]. Studying of the filter with three-dimensional positioned fiber and the diameter of the fiber to d=19 μm by Qiqi Wang (2007) [6]. Studying of manufacture a filter with a diameter of up to 900 nm by Zheng Jie-Long Yun-Ze (2012) [7].

Synthetic polymers provide greater flexibility in their filtration properties compared to fiberglass. Polymer fibers have demonstrated a significant development in filters in terms of efficiency, size of retained particles, resistance and ability to retain dust particles. They also have mechanical properties such as high resistance as well as low environmental impact in terms of energy use and residues [8-9]. Figure (1) shows the filter fibers of the rank nanometer and micrometer.

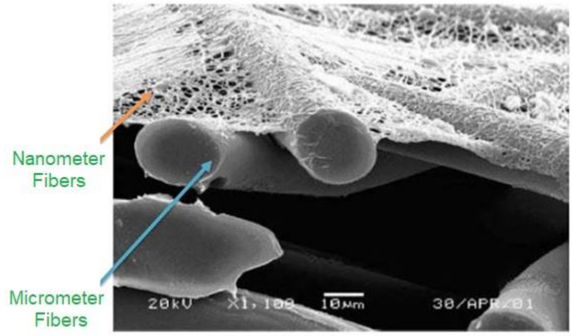

Figure 1. shows the filter fibers nanometer and micrometer.

2. Method of manufacturing nanofibers using electrospinning

Fiber by definition is a cylindrical shape of a diameter much smaller than its length, where experiments have shown that a certain electric charge can make a fiber after being applied to a drop in the nozzle and overcoming its tensile strength [10].

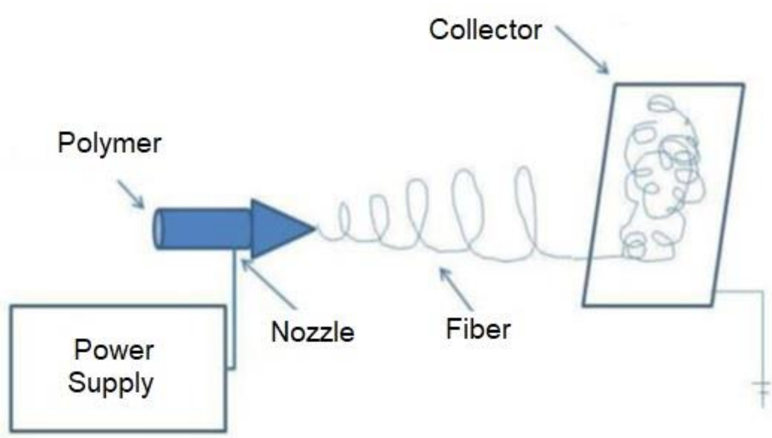

Figure 2. is a schematic diagram of the method of manufacturing fibers using electrospinning.

The voltage is initially applied to the polymer solution and the droplets are formed on the surface of the hemispherical needle. As the voltage increases, the shape of the drop on the surface changes from hemispherical to spherical and eventually becomes conical. It is called the Taylor cone [11], and is shown in Figure (3).

Figure 3. Taylor cone.

At a certain electrical charge, the surface tension is overcome and the fiber is formed towards the collector. The diameter of the fibers is determined by many variables, the most important of these variables is the type of polymer, its molecular weight and the percentage of solvents required to obtain the solution. These fibers form a large area due to their small diameter and can produce filters with small pore sizes, thus improve the efficiency of the filters from penetration of fine particles Figure (4) shows how fiber is formed [12,13].

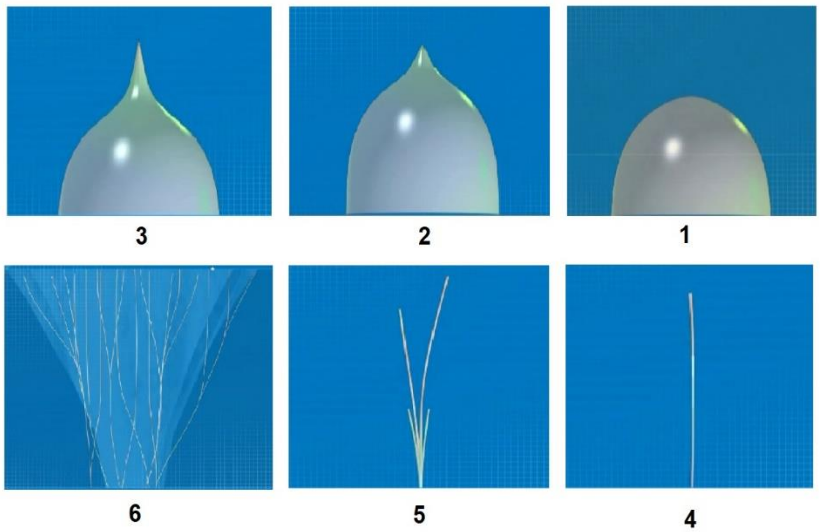

Figure 4. shows how fiber is formed

3. Variables of the fiber manufacturing process and its impact

3.1 Electrical voltage

Voltage plays the role of a pump in the movement of liquids in an electrospinning method, creating a similar pressure drop between the source and the collector. When the end of the voltage is connected to the fluid, the charge begins to accumulate on the surface of the fluid opposite the other end. As the voltage increases, the strength of the electric field increases and the charge accumulated on the surface of the fluid increases. This will lead to fluid flow and may affect the stability of the Taylor cone. When the fluid speed increases, the path time between the source and the collector is reduced, which means that the fluid must solidify during this short period of time [14].

3.2 Flow rate

According to the continuity equation:

$$Q = \rho . V . A \qquad (1)$$

Where:
Q: Mass flow of jet.
ρ: Mass density of jet.
V: Velocity of jet.
A: Area of the jet.

If the flow increases, the diameter of the jet will increase, provided that all other conditions remain the same, but with some conditions. As the flow rate increases, the applied voltage should be increased to maintain a constant flow rate at the nozzle. This will increase the velocity of the jet and reduce its diameter. Whether or not the diameter of the jet will increase or decrease depends on the balance between the change in voltage and the flow rate [15].

3.3 Nozzle diameter

When the diameter of the nozzle is minimized, the diameter of the fluid decreases and therefore the surface tensile strength is increased, requiring a stronger electric field. The electric field can be increased either by decreasing the distance between the source and the collector or by increasing the voltage as shown in the following equation:

$$E = \frac{V}{L} \tag{2}$$

Where:
E: Electric field intensity.
V: Applied voltage.
L: The distance between the source and the collector.

4. filtration standard

The filter efficiency classification is based on the Minimum Efficiency Rated Value (MERV) classification system developed by the American Association of Refrigeration and Air Conditioning Engineers (ASHRAE) American National Standards Institute (ANSI) and documented in ANSI, ASHRAE 52.2-2007 and ANSI, ASHRAE 52.2- 2017 for a test methods [16,17].

This International Standard specifies test methods for determining filter efficiency, which are classified according to the diameter of the molecule to be reserved where the diameter ranges from (0.3-10) µm. The smaller the particle diameter, the more efficient the particulate filter is to be removed. The MERV classification system allows comparing the efficiency of filters in particle removal in one of three areas:

$(0.3 - 1)\mu m.$
$(1 - 3)\mu m.$
$(3 - 10)\mu m.$

The ANSI, ASHRAE 52.2 standard explains how the molecular size range (0.3-10) µm has been determined to test filters. The upper limit of 10 µm was chosen because molecules of this size could cause health problems if they passed through the airway. Molecules larger than 10 µm are unlikely to remain in the airway long enough to make them in the filter so these molecules are neither considered nor tested against the ANSI, ASHRAE 52.2 classification system. However, molecules with a diameter of about 10 µm are known to cause problems in mechanical equipment as it accumulates in coils leading to biological growth and corrosion in coils [18, 19].

The minimum amount of 0.3 microns was chosen due to the commercial availability of equipment that can calculate particles of this size. The lower MERV rating filter may be acceptable in some applications. Given the importance of the size field for (cleanrooms - operating rooms ...).

These relative efficiencies are equivalent to the declared efficiency in the National Air Filtration Association (NAFA) for installation, operation and maintenance of air filtration systems [20,21].

Based on the above, different filter types and MERV fields are recommended ANSI, ASHRAE 52.2. Table (1) provides a list of applications where different particle size and MERV filters are selected and shows that less severe applications such as residential applications and some commercial applications use lower MERV filters while air-critical applications Health facilities and operating theaters have higher rated MERV filters.

Table 1. Applications in which different filters are selected relative to particle size and MERV

MERV	Particle Range	Filter Type	Applications
1-4	$> 10\ \mu m$	Disposal panel	Minimum residential filtration, window AC units
5-8	$3.0 - 10\ \mu m$	Pleated or disposal panel	Commercial buildings, better residential filtration, industrial workplaces
9-12	$1.0 - 3.0\ \mu m$	Bag	Superior residential, better commercial filtration, hospital laboratories
13-16	$0.3 - 1.0\ \mu m$	Bag	Superior commercial, general surgery, hospital inpatient care
17-20	$\leq 0.3\ \mu m$	HEPA/ULPA	Cleanrooms, pharmaceutical manufacturing, locations with carcinogenic or radioactive materials, orthopedic surgery

5. Determination of the physical properties of the polymer

5.1 Temperature and humidity

The properties of PEO and PU are affected by climatic conditions such as ambient temperature and humidity. Experiments on the PEO can be carried out under all climatic conditions (summer or winter) since the solvent used for the polymer is water, but in this case the viscosity of the fluid changes. Whereas there is a difficulty to conduct an experiment on the PU in the summer time because the solvent used is acetone, where acetone is rapidly evaporating so the solution must be cooled.

Both the temperature and humidity affect the diameter of the fibers, controlling the evaporation rate of the solution; affect the continuing formation of fibers so fibers can reach the collector with a lower diameter.

5.2 Concentration of solution

Several concentrations of the PEO polymer were considered within the solution ranging from (4-6-8-10-12) %. Experiments showed that a concentration of 6% of the PEO produced nanofibres below 300 nm, where 6 gr of PEO versus 94 gr of water solvent were mixed under a temperature of $(40 - 60\ ^\circ C)$ in an oven for 24h until the solid polymer was turned into a viscous fluid. For the polymer PU (4-6-8-10-12)% ratios were applied. Experiments showed that a concentration of 10% of the PU produced nanofibres below 300 nm, where 10 gr of PU versus 90gr of acetone solution were mixed until the solid polymer turned into a fluid viscous.

5.3 Density of the fluid

The volumetric mass of the fluid was calculated using a $1cm^3$ syringe weighed empty and then the volume of $1cm^3$ was taken from the fluid and weighed and the density calculated as in Table (2).

Table 2. Calculate the density of fluid PEO, PU

Fluid type (Cm^3)	Empty weight (gr)	The weight complete (gr)	Net weight (gr)	Density ($\frac{Kg}{m^3}$)
6% PEO + water	2.025	3.010	0.985	985
6% PEO + water	2.005	3.011	1.006	1006

8% PEO + water	1.993	3.012	1.019	1019
8% PEO + water	1.997	3.010	1.013	1013
10% PEO + water	2.159	3.219	1.060	1060
10% PEO + water	2.150	3.216	1.066	1066
6% PU + Acetone	2.025	2.944	0.919	919
6% PU + Acetone	1.986	2.942	0.956	956
8% PU + Acetone	1.992	2.956	0.964	964
8% PU + Acetone	1.991	2.961	0.97	970
10% PU + Acetone	1.989	2.976	0.987	987
10% PU + Acetone	1.997	2.979	0.982	982
12% PU + Acetone	1.987	2.993	1.006	1006
12% PU + Acetone	1.992	3.018	1.026	1026

5.4 Viscosity of the solution

The dynamic viscosity µ is calculated as follows by Stocks law:

$$\mu = \frac{2}{9} \times r^2 \times g \left(\rho_{pb} - \rho_{liquid} \right) \times \frac{t}{d} \qquad (3)$$

Where:
R: The radius of the lead ball is 1.66 mm.
ρ_{pb}: lead density is 11300 kg/m^3.
t: Time of the fall of the ball in the solution (Sec).
d: Fall distance (m).

Table 3. Calculated of viscosity PEO, PU.

Fluid	Distance (cm)	Time (sec)	Density ρ ($\frac{Kg}{m^3}$)	Viscosity µ ($P_a.sec$)
6% PEO + water	3	2.52	985	5.27
6% PEO + water	3	2.49	1006	5.13
8% PEO + water	3	7.75	1019	15.95
8% PEO + water	3	7.81	1013	16.08
10% PEO + water	3	27.5	1060	56.38
10% PEO + water	3	27.43	1066	56.20
6% PU + Acetone	3	3.6	919	7.48
6% PU + Acetone	3	3.9	956	8.07
8% PU + Acetone	3	4.4	964	*9.10*
8% PU + Acetone	3	4.8	970	*9.92*

10% PU + Acetone	3	6.3	987	*13.01*
10% PU + Acetone	3	6.1	982	*12.60*
12% PU + Acetone	3	7.6	1006	*15.66*
12% PU + Acetone	3	7.9	1026	*16.25*

6. Experimental results

A number of experiments were carried out on the PEO, PU polymer solution. Both the voltage and the distance between the source and collector were controlled and nanometer filters were prepared, and measure the diameter of the fiber on the Scanning electron microscope (SEM). We have reached the results shown in the table (4).

Table 4. Measurement results PEO, PU.

Sample	Fluid	Distance (cm)	Electrical voltage (k)V	Temperature and humidity	Diameter (nm)	Time (sec)
1	6% PEO + water	10	10	45% - 41°C	751	30
2	6% PEO + water	12	12	44% - 40°C	478	30
3	6% PEO + water	14	14	40% - 41°C	282	30
4	6% PEO + water	15	15	42% - 38°C	272	30
5	6% PEO + water	16	16	40% - 35°C	196	30
6	6% PEO + water	17	16	41% - 37°C	195	30
7	6% PEO + water	17	17	42% - 38°C	144	30
8	6% PEO + water	18	18	42% - 41°C	119	30
9	6% PEO + water	18	20	40% - 36°C	109	30
10	6% PEO + water	20	22	41% - 34°C	97	30
11	6% PEO + water	21	24	40% - 34°C	77	30
12	6% PEO + water	22	26	40% - 32°C	40	30
13	8% PU + Acetone	16	16	40% - 40°C	398	30
14	10% PU + Acetone	12	14	40% - 38°C	219	30
15	10% PU + Acetone	14	14	42% - 37°C	213	30
16	10% PU + Acetone	15	15	43% - 32°C	200	30
17	10% PU + Acetone	18	18	44% - 31°C	106	30
18	10% PU + Acetone	20	20	40% - 32°C	100	30

Figure (5,6,7,8) show the relationship between the distance between the source and the collector and the electrical voltage with the diameter of the fiber.

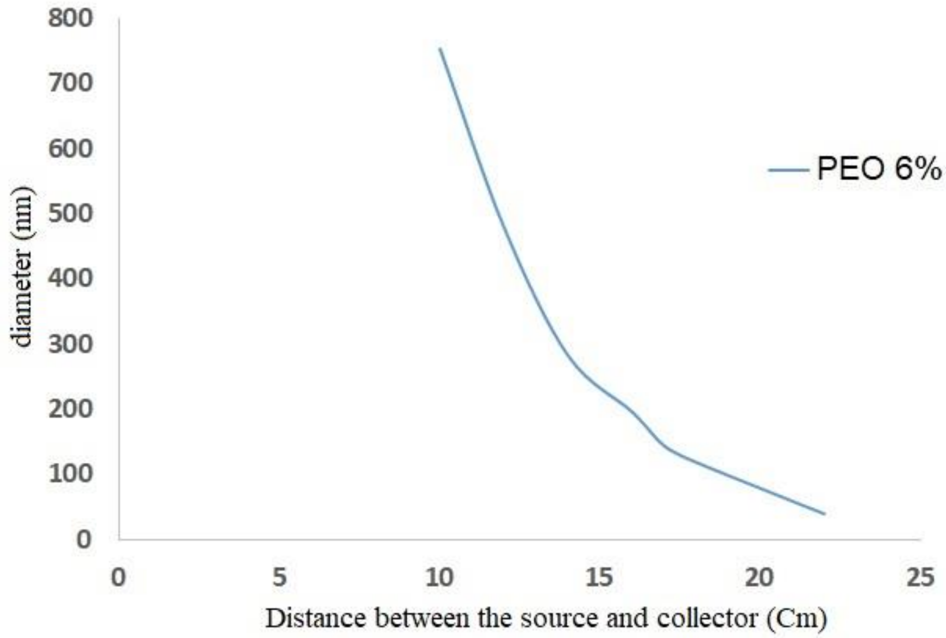

Figure 5. shows the relationship between the distance between the source and the collector with the diameter of the fiber PEO.

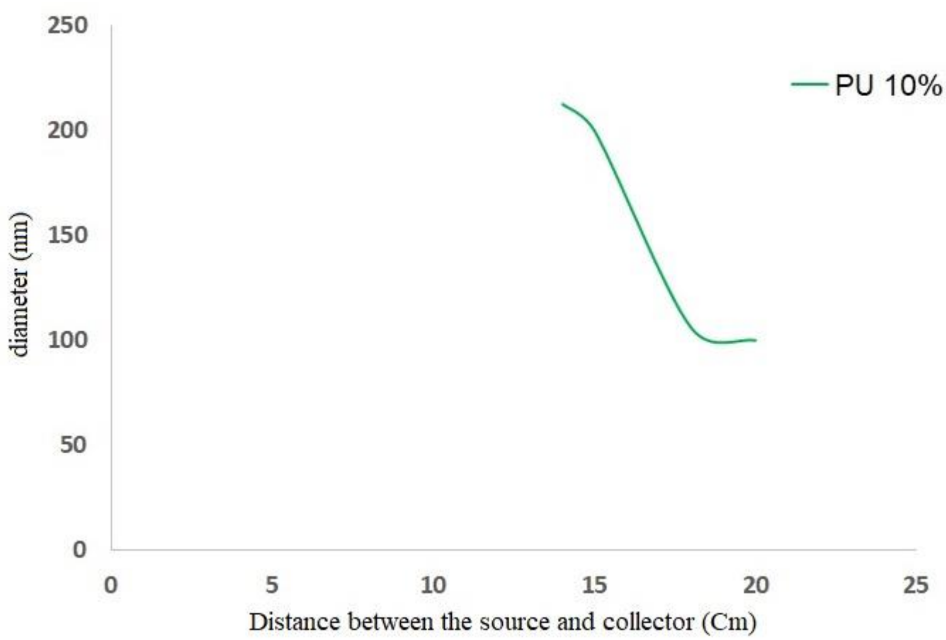

Figure 6. shows the relationship between the distance between the source and the collector with the diameter of the fiber PU.

From Figures (5,6) The larger the distance between the source and the collector, the smaller the diameter of a nanofiber.

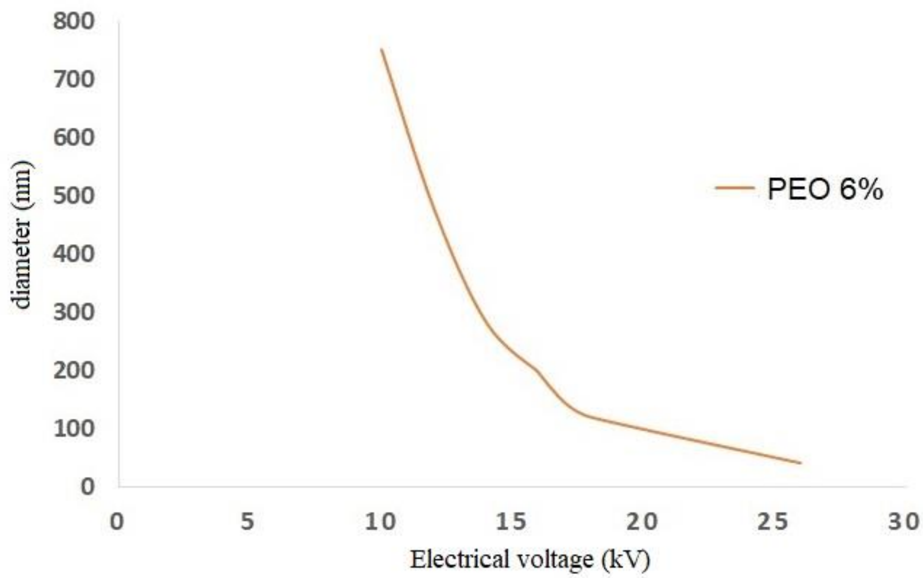

Figure 7. shows the relationship between the electrical voltage with the diameter of the fiber PEO.

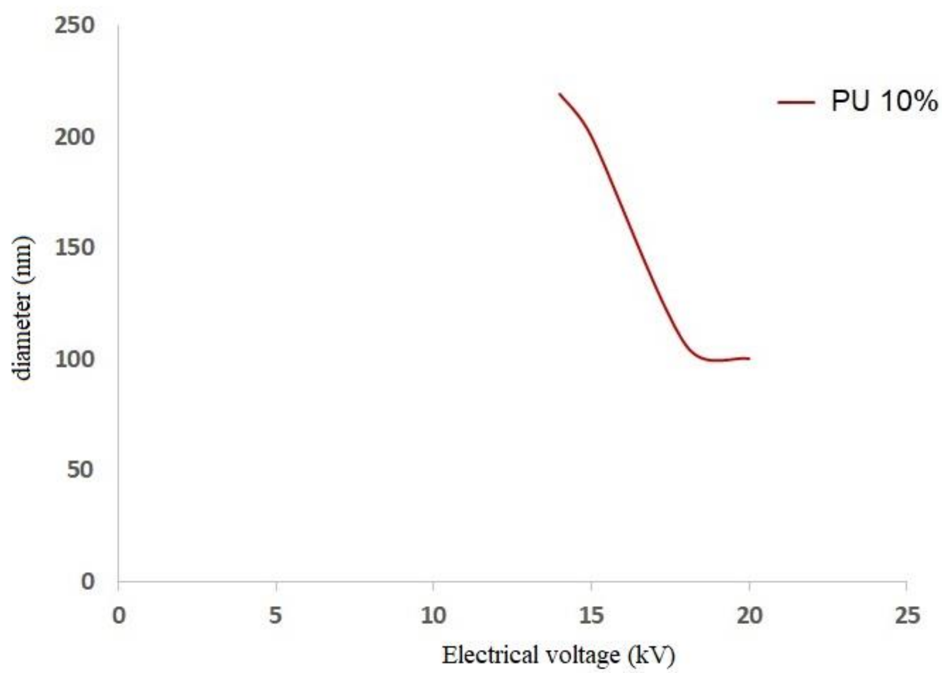

Figure 8. shows the relationship between the electrical voltage with the diameter of the fiber PU.

From Figures (7,8) The larger the voltage, the smaller the nanofiber diameter.

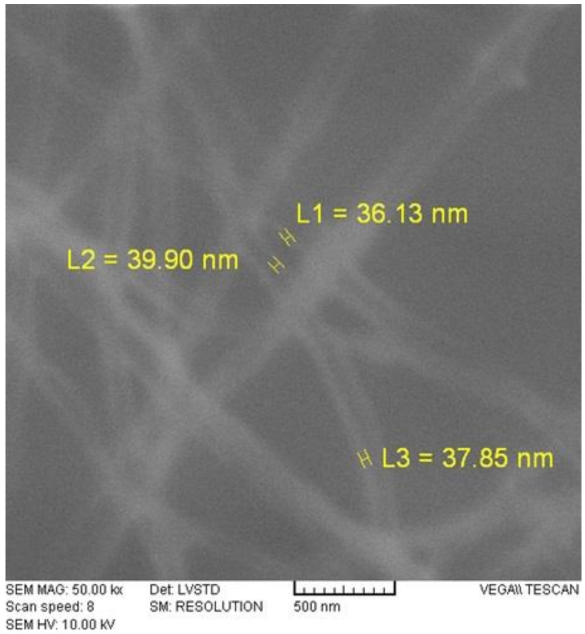

Figure 9. is a nanofibers diameter about 40 nm measured on the SEM electron microscope of (PEO) manufactured by the method of electrospinning at a concentration of 6%. The distance between the nozzle and the collector is 22 cm, the voltage is 26 kV, the temperature is 32℃, the humidity is 40% and the operating time is 30 S.

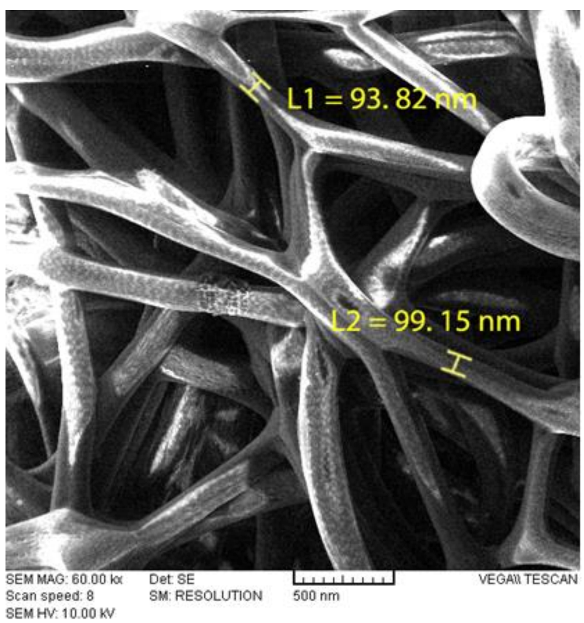

Figure 10. is a nanofibers diameter about 100 nm measured on the SEM electron microscope of (PU) manufactured by the method of electrospinning at a concentration of 10%. The distance between the nozzle and the collector is 20 cm, the voltage is 20 kV, the temperature is 32℃, the humidity is 40% and the operating time is 30 S.

7. Filter test

The filter was tested by exposure to nanometer diameter bacteria. Escherichia coli was selected. The presence of these bacteria in the surrounding environment as a result of fecal contamination indicates that infection with these bacteria leads to intestinal bleeding and diarrhea of varying severity.

E. coli is an organism-shaped bacteria that is not visible to the naked eye like all bacteria, 2 microns in length and 0.5 microns in diameter. Figure (11) shows the E. coli form.

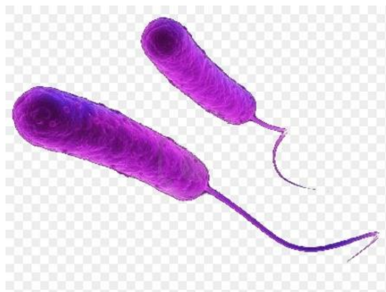

Figure 11. shows the E. coli form.

Several experiments were carried out in the Laboratory Medicine Department of Aleppo University Hospital on 10 filters as shown in Fig (12), where E. coli bacteria were transplanted to the surface of the filter at a temperature of 37℃ for 24 hours per filter. The samples were examined by taking more than one swab on the second face for the planting place. It was found that there was no penetration of the filter for the ten samples.

Figure 12. Shows the tested filter.

8. Conclusion

The PU polymer has been selected as a better material to manufacture filters than PEO, because PEO solvent is water which leads to the disintegration of its fiber at high humidity. Whereas, the solvent of PU is acetone which does not disassemble the nanofibers at high humidity.

Based on the above, the previous filter can be used in the Air Handling Unit and in the air vents entering the operating theaters and the patient's rooms. It is within the range (0.3-1) μm. Hence, a high efficiency filter with a MERV score above 13 is equivalent to the declared efficiency in the installation, operation and maintenance of NAFA air filtration systems and ANSI, ASHRAE 52.2.

9. References

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