Preparation and Study of some Physical Properties of (Polystyrene/Ethyl vinyl acetate) Blend Nanofibers

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Abstract:
This search aims to fabricate immiscible nanofibers (Polystyrene/Ethyl phenyl acetate) blends with different average porous for different applications by electrospinning technique. PS and EVA were mixed by (50/50) to prepare 0.1 (w/v) con.%, each polymer dissolved in (Tetra hydro furan ). Resulting nanofibers morphology was studied by Atomic force microscopy (AFM) and high optical resolution microscope (HORM) , Contact angle between the water and the surface of nanofibers by contact angle analyzer also studied for (hydrophilic or hydrophopic behavior ). FTIR test for checking the emergence or not of new bonds in the nanofibers blend was performed.

AFM Results showed that the prepared blends of (PS+EVA) have homogenous needle structures (nanofibers) at three dimensions , while the results of (HORM) shows the nonwoven structures contain intermediates pours structure , Contact angle results show that decrease of the contact angle after adding the EVA polymer to PS, and this refers to the (EVA/PS) nanofibers blends have hydrophilic behavior.

Key words: Porous nanofibers, blends nanofibers, nano filter, electrospinnnig.

1. Introduction
Polymeric nanofibers have acquired a great interest in the scientific fields for their importance in the nanotechnology, biotechnology, and other related technologies.(Wendorff et.al., 2012 ; Al dabbagh & Alshimary 2016)

Nanofibers have many superior properties that make them superior to many other materials for use in sensitive areas, particularly within the areas relevant to the lives and health of living organisms and medical, industrial . In addition that nanofibers are used in molecular filtration, tissue engineering, drug delivery, wound dressing, cosmetics, solar and fuel cells, bio and nano sensors, etc. (Asmatulu et.al., 2013 ; Ayse, 2009; Muppalla, 2011).

Nanofibers have extremely high surface to weight ratio compared to traditionalism
	nanowovens. large surface area to mass .Low density, high pore volume, and tight pore size make the nanofiber nonwoven appropriate widely in filtration applications.( Anthony , 2008)
Generally, polymeric nanofibers are produced by Electrospinning technique (Figure 1). Electrospinning is a process that prepares fibers with diameters ranging from 10nm to some hundred nanometers. (Ji-Huan et. al., 2008).

![Fig (1) electrospinning process](image)

When a sufficiently high voltage is applied to a liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion overcome the surface tension and the droplet is stretched; at a critical point a stream of liquid erupts from the surface. This point of eruption is known as the Taylor cone.

Electrospinning technique is the best method for producing high control nonofibers with high porous density. (Hale, 2014)

2. Experimental Part:

1.2 Materials and Methods

Polystyrene (PS) \[C_8H_8\] as white transparency granules with glass transition temperature: 100°C, density 1.05 g/cm$^3$ at 25°C, and purity is 99.95%, India product was used.

Ethyl vinyl acetate \[(C_2H_4)n(C_4H_6O_2)m\] 18% content used for nanofibers blending (EVA/PS) preparation, India product.

Tetra hydro furan (THF) used as a solvent, it has Boiling point \(T_B=66\,^\circ\text{C}\). It was obtained from (Qualikems Fine Chem. Pvt. Ltd) Nandesari, Vadodara, India.

2.2 Electrospinning solution preparation:

Two samples were prepared, in this search as shown in table (1):

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS 100%</td>
</tr>
<tr>
<td>2</td>
<td>PS + EVA (50/50)</td>
</tr>
</tbody>
</table>
The spinning condition of samples are: Con.% : 0.1 w/v, H.V: 18 kV, I. R.: 0.3 ml/hr, D: 10 cm, N.D: 0.48 mm, Time: 2 hr.

3.2 Electrospinning set up:
Electrospinning system consist of three main elements:
- a. Direct high voltage power supply with (0-50 kV) range.
- b. Metallic collector: stainless steel rotates cylinder collector with (10 cm as a diameter and 20 cm as a length).
- c. Syringe pump with medical syringe (0.48 mm Needle Diameter).

Fig (1) shows the typical connect of electrospinning setup, (+ H.V) connect with metallic needle, while (- H.V) connected to earthly collector which parallel to syringe pump. Table (2) shows the elements of electrospinning system with function of each of them.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Function</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>High voltage power supply</td>
<td>Generate a high voltage to overcome the surface tension of polymer solution and start the Taylor cone.</td>
<td>0-50 kV</td>
</tr>
<tr>
<td>Syringe pump</td>
<td>Controlled the flow rate of polymer solution at different range.</td>
<td>0.1 – 999 ml/hr.</td>
</tr>
<tr>
<td>Metallic collector</td>
<td>Collects the resultant nanofibers</td>
<td>rotate with (0-3000 rpm)</td>
</tr>
</tbody>
</table>

4.2 Tests:
Table (3) shows the all tests which are performed at this search with the purpose of each test:

<table>
<thead>
<tr>
<th>Tests</th>
<th>Machine</th>
<th>Purpose of test</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR</td>
<td>SHIMADZU FTIR analyzer</td>
<td>Known of new bonds</td>
</tr>
<tr>
<td>Contact angle</td>
<td>Contact angle analyzer</td>
<td>Test the behavior of nanofibers textile (hydrophilic or hydrophobic)</td>
</tr>
<tr>
<td>AFM</td>
<td>Nanosurf LensAFM</td>
<td>Study of morphology of nonwoven</td>
</tr>
<tr>
<td>HROM</td>
<td>Grayfield Optical Inc.</td>
<td>Study the morphology and porous structure of nonwoven</td>
</tr>
</tbody>
</table>

3. Results and discussion:
1.3 FTIR Test
Fig (2 a,b) show the data chart of FTIR test for two sample, fig (2, a) show the FTIR analysis of (PS nanofibers), notice from this analysis there are an aromatic C-H bending at range about (600 – 800 cm⁻¹), also there are an aromatic (C=C) bending at 1672.28 cm⁻¹, also the PS nanofiber’s spectrum showed the principal peaks of mono-substituted aromatic hydrocarbon, such as C-H stretching at 3900 cm⁻¹; overtone and combination bands at 2331.94 cm⁻¹. Fig (2, b) shows the FTIR analysis of (PS/EVA blend nanofibers). We show from these figs, there is a new bonds present after blending the PS with EVA such as (C=O) stretching, also notice from two curves there are an shifting in the original bonds of PS nanofibers, The results from FTIR demonstrated that PS was interconnected with EVA through hydrogen bonds in the macromolecular region. (Todsapon et.al., 2014)
2.3 Contact angle

Table (4) show the contact angle of all samples:

<table>
<thead>
<tr>
<th>Sample (1)</th>
<th>Contact angle °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum foil</td>
<td>55</td>
</tr>
<tr>
<td>Aluminum foil coating by PS nanofibers</td>
<td>~ 90</td>
</tr>
<tr>
<td>Aluminum foil coating by PS/EVA (0.5:0.5) nanofibers</td>
<td>77</td>
</tr>
</tbody>
</table>

Fig (3) shows the contact angle of three samples. Noticed from the table (4) and fig (3) the contact angle of aluminum foil is the lowest value about (55 °), while the contact angle of (Al+ PS nanofibers coating) increase to (~ 90°), this is because the hydrophobic behavior of PS nanofibers. (Al dabbagh & Alshimary 2016)

Also noticed the contact angle of (Al + PS/EVA blend nanofibers) is lower than the sample with PS coating, this refers to, the surface property changing from hydrophobic to hydrophilic and this is supposed to improve the filtration process (higher filtration kinetics) by making it easier and faster and preventing the blocking of the nanofiber membranes (Ramazan, 2013)

Figs (4 a,b,c) show the analyzer images of contact angle of three samples [(Al), (Al coating by PS nanofibers), and (Al coating by PS/EVA blend nanofibers)].

3.3 Morphology Results:

3.3.1: AFM Results:

Fig (5 a, b) show the morphology of nanotextile coating at three dimensions, noticed that the electrospinning coating has a homogeneity nanofibers structure at all dimension as in Fig (5 a) which show the PS coating morphology, while the fig (5 b) show the nano structure of (PS+EVA) blend nanofibers. we notice there are a porous structure on the surface of (PS+EVA) nano coating. This is because immiscibility of this blend and this lead to a phase separation occurring between its elements which lead to porous structures.

3.3.2: HORM Results:

Fig (6 a, b) show the optical images of surface of nanotextile coating, noticed that the electrospinning coating has a homogeneity nanofibers surface as in Fig (6 a) which show the PS coating morphology, while the fig (6 b) show the surface of nano (PS+EVA) blend nanofibers. Notice there are a porous structure on the surface of (PS+EVA) nano coating. This is because immiscibility of this blend and this lead to a phase separation occurring between its elements which lead to porous structures.

Conclusion:

We conclude from this search:
1- Can prepare hydrophilic nanotextile by blending electrospun nanofibers.
2- Can control the porous structure in this nanotextile sample for filter application.

References:


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Fig (2, a) FTIR analysis of (PS) nanofibers

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Fig (2, b) FTIR analysis of (PS/EVA) blends nanofibers

Fig (3) shows the contact angle of three samples
Fig (4) shows the contact angles analyzer images for all samples: a- Al foil  b- Al foil coating by PS nanofibers  c- Al foil coating by PS/EVA blend nanofibers.

Fig (5.a) Nano PS coating

Fig (5.b) Nano (PS+EVA) coating

Fig (5 a,b) shows the AFM images of coating.
a. AFM morphology of PS nanocoating  
b. AFM of PS+EVA nanocoating

Fig (6.a) Nano PS coating

Fig (6.b) Nano PS coating

Fig (6 a,b) show the optical images of surface of coating

a. Surface morphology of PS nanocoating  
b. Surface morphology of PS+EVA nanocoating