Studying the Effect of some Parameters on PS Microfibers by Electrospinning Technique

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Abstract :

The aim of this search is prepared and study of PS/(CL.F0.5+DMF0.5) Microfibers by electrospinning technique under different working condition including solution parameters such as (solvent, viscosity, concentration, conductivity, surface tension) and set up parameters including (voltage, flow rate) .

Results show the diameter of micro fibers decreased with increasing of voltage value, conductivity of media solution. While the Microfibers diameter increased with increasing of (viscosity, flaw rate, tip diameter, and concentration of solution) .

AC- HV leads to higher diameter than DC-HV but with more alignment of Microfibers.

Key word: electrospinning, Microfibers, cylinder rotate collector, working parameters

الخلاصة :

الهدف من هذا البحث تحضير ودراسة الياف البولي ستايرين المذاب في مزيج من الكلوروفورم و داي مثيل فورما اميد بنسبة (0.5:0.5) المايكروية المحضرة بواسطة منظومة الغزل الكهربائي تحت ظروف عمل مختلفة تشمل ظروف خاصة بالمحلول مثل (المذيب، اللزوجة، التركيز، التوصيلية، والشد السطحي) ، وكذلك ظروف خاصة بتنصيب المنظومة وتشمل (الفولتية، نسبة الضخ)

اثبتت النتائج ان قطر الليف يقل بزيادة الفولتية وتوصيلية المحلول ، كما ان قطر الليف يزداد بزيادة كل من (اللزوجة ونسبة الضخ وتركيز المحلول) .

كما اثبتت النتائج ان الفولتية المتناوبة تؤدي الى قطر ليف اكبر من الفولتية المستمرة لكن مع اصطفاف اكبر للالياف المايكروية.

الكلمات المفتاحية: الغزل الكهربائي، الياف مايكروية ، هدف دوار اسطواني، متغيرات العمل.

Introduction:

With the rapid development in Nano science and Nanotechnology over the past two decades, great progress has been considered not just in the preparation and characterization of Nanomaterial, but also in functional applications. Nano materials as a one-dimensional significant, Nano fibers have high specific surface area due to their extremely small diameters, and Nano fiber membranes, which are highly porous with perfect pore bonding. This unique properties as well as functions of the polymers themselves transported Nano fibers with Many of the desirable properties for advanced applications.[Jian *et al*., 2011] Nano fibers have applications in medicine, including artificial organ components, tissue engineering, implant material, drug delivery wound dressing, and medical textile materials. [Naji *et. al*.,2011] Also, Nano fibers are used in protective materials including sound absorption materials, protective clothing against chemical and biological warfare agents, and sensor applications for detecting chemical agents. Nano fibers have also been used in pigments for cosmetics applications in the textile industry include sport apparel, sport shoes, climbing, rainwear, outerwear garments.

In 2003 Lee et al studied the effect of concentration, applied voltage, and tip-collector distance on the diameter of polystyrene/THF,N,N-DMF resulting Nano fibers, the PS Nano fibers produced contained irregular beads and electro spinning certainly was enhanced with increasing of DMF solvent, also the beads and the Nano fibers diameter increase with increasing of polymer concentration. While THF solvent led to an unexpected half hollow spheres (HHS).[Lee, 2003].

Also, Sachiko *et. al*., studied the effect of electro spinning parameters on the morphology and fiber diameter of regenerated silk from Bombyx mori. Effects of electric field and tip-to-collector distances of various silk concentrations in formic acid on fiber uniformity, morphology and diameter were measured. Results showed that the silk concentration was the most important parameter in producing uniform cylindrical fibers less than 100 nm in diameter. [Sachiko *et. al*., 2003]

In 2007 Goki E. *et. al*. studied the morphology transition, namely bead-to-fiber transition, of electro spun polystyrene, with its molecular weight ranging from 19,300 to 1,877,000 g/mol. Tetrahydrofuran and N,N-dimethylformamide were used as solvents to examine the effects of solvent properties on the morphological diversity. Polymer molecular weight and solvent properties had a significant impact on the morphology of beads as well as Nano fibers. Notice of fiber diameter and its distribution proposed that the effect of molecular weight and solvent may be independent. The critical concentrations at which primary and complete fibers were observed and were found to significant reduction with molecular weight, as can be expected. The effect of solvents on these critical concentrations was lower for mid to high-molecular-weight (>100,000 g/mol) solutions. Rapid solidification of jet which was expected to occur with concentrated solutions may play a vital role in establishing stable fibers during electro spinning. [Goki *et. al*.,2007].

Tan *et. al*.(2008) . a scanning electron microscope (SEM) was used for studying the morphologies and microstructures of the electro spun micro/Nano fibers .The micro/Nano fibers prepared by the typical electro spinning were usually collected in the form of non-woven mats lacking of structural orientation. However, by modifying collector of the electro spinning setup, the resulting polymer fibers showed aligned structures to some extent. In this study found that the electrostatic force originating from the splitting electric field plays a key role in the alignment of the micro/Nano fibers.[Tan *et. al*., 2008].

In 2013, Z. Li *et. al*., showed the effecting of working parameter on resultant Nanofabers from electrospinning technique. Those parameters can be broadly divided into three parts such as solution parameters incloding (Concentration, Molecular Weight, Viscosity, Surface Tension, and Conductivity/Surface Charge Density), process parameters incloding (Voltage, Collectors, Flow Rate, and Distance (H) Between the Collector and the tip of the syringe, and ambient parameters incloding (humidity and temperature. Each of those parameters can affect the fibers morphologies and by proper control of those parameters we can fabricate electrospun fibers with desired morphologies and diameters.[Lie *et. al*.,2013] In 2014, N.H.A. Ngadiman *et. al*. presented a review of effecting parameters through the electrospinning technique concentration, spinning distance, and applied voltage, and volume flow rate, to the Nanofiber diameter during electrospinning process. It was concluded that fiber volume flow rate was proportional to fiber diameter while there was no agreement in reports on other parameters. [Ngadiman *et. al*., 2012]

Experimental parts:

Materials and method:

1- Polystyrene (PS): $(C_8H_8)_n$ was used as another material to produce polystyrene Nano fibers, with average molecular weight of M_w 290,000 as translucent white granules of 1.05 g/mL density at 25 °C was purchased from Iran Petrochem Institute.

2-Dimethyleformamide (DMF), Tetrahydrofuran (THF), Chloroform (CL.F), and Ethanol (Eth.) as a solvents were used as in table (1).

3- Nano-azma electrospinning system was used for preparation of Microfibers, Iranian company , Tehran university.

4- four digits microbalance and magnetic starrier were used for preparation of electrospinning solutions.
5- SEM was used for to study the morphology and diameter of Microfibers, DSC used for studying of crystallinity of Microfibers.
6-AC-high voltage (15 kV) , Thailand company.
7- Tensometer: This tool used for measurement of surface tension of solvent and solution that used at this research, this tools type (JYW-200 A) from LARYEE Chain manufacture company) .

Table 1. shows the solvents and concentration which used at this search.

Polymer type	Solvent type	Percentage of solvent	Concentrations w/v
PS	THF	100%	0.1
	DMF	100%	0.1
	DMF+THF	0.25+0.75	0.1
	DMF+CL.F	0.25+0.75	0.1
		0.75+0.25	0.1
		0.5+0.5	0.09
			0.1
			0.13
			0.15
	DMF+CL.F+Eth.	0.5+0.3+0.2	0.1

Result and discussion :

Fig 1. Showed the effect of concentration on viscosity and surface tension of (PS/0.5 DMF+0.5 CL.F) solution :
From figures notice that the surface tension and viscosity of solutions increased with increasing of solution concentration. Solution concentration and surface tension are closely correlated factors, this because the high concentration mean higher number of polymer chains in solution and this may lead to an increase of the viscosity and the surface tension and vice versa.

Fig 2 (a-d). Showed the microscopies images of PS/0.5 DMF+0.5 CL.F Microfibers under (AC- 15kV, 7 cm distance, 1 ml/hr injection rate , 0.89 mm Needle diameter, and 360 rpm rotate speed of collector for all concentrations of solutions include (0.09. 0.1, 0.13, & 0.15%).

1- For low concentration << (0.09 w/v) where the solutions have low viscosity and surface tension , the product would be polymeric particles as electrospray droplets [Deitzel 2001].
2- Upon increasing the solution concentration > (0.09 w/v) it was found that the product become a mixture of beads and Microfibers with fibers diameter about 156 nm, the presence of beads is believed to be due to the axisymmetric instabilities in the jets flow. [Eda,2005].
3- When an appropriate concentration, (0.13% con.), the product was a smooth and uniform Microfibers, but with no beads and bigger Nano-diameter (703 nm) [Fong et al 1999 & Lee *et. al*., 2003].
4- Upon increasing concentration to (0.15%)con. w/v the Microfibers diameter increased to (1094 nm) with no beads.[Li *et. al*., 2004]

Fig (3a-g). the effect of solvent on PS Microfibers diameter and morphology, under 1 ml/hr I.R, , 360 rpm R.S, 15 kV-AC , 7 cm distance , N.D=0.89 mm, and con. w/v =0.1w/v

Using of a DMF as a solvent for PS, leads to produce microfibers with (2200 nm), very little porous, and without beads, because this the resulting solution (DMF+PS) yield a very broad distribution of fibers diameters. Because this media had electrical conductivity (1.08 μS/cm) ,and dielectric constant (31.8), and high surface tension (16.38 mN/m) . However the microfibers diameter were controlled by changing the composition ratios of solvent media, such as adding other solvent to THF like DMF [Mohammed et. al 2010] , the other parameters such as solution and working parameters can control the beads. Fig (3a)

1- THF alone with under the same previous condition of (DMF) at step 1 gives a Microfibers with lower diameter than (DMF), up to (860 nm), although the DMF has high electrical conductivity and high dielectric constant but it gives an poor microfibers because it has high boiling point (153^{o} C), while the THF solvent with dielectric constant (7.6) and electrical conductivity about (0.15 μS/cm) is a good for electrospinning of microfibers because it has low boiling point (56^{o}C). [Wannatong *et. al*., 2004] , Fig (3.b).
2- When we change the solvent media by added some other solvent with different ratios such as: we mix the (0.25 DMF +0.75 THF), this mixture leads to decrease microfibers diameter about (560-1840nm), this is because there is an changing in electrical conductivity of the mixture (1.1 μS/cm) and an decreasing of the surface tension is happened up to (13.76 mN/m), these changes in solvent media properties lead to an high affectivity by applied electric field then it leads to reduction of the microfibers diameter.
   Also we notice some of porous prune-like beads appeared with this solvent media because there is an instability jets through electrospinning process. Fig (3.c)
3- With changing of the solvent media to (0.75 DMF + 0.25 CL.F),this ratios of tow solvent leads to produce an media with (1.9 μS/cm) electrical conductivity and (16.88 mN/m) surface tension, this solution leads to produce a microfibers with (690-2580 nm), but the evaporation point of this mixture is higher than the previous media, for this reason, there is an increasing of microfibers diameter was happened [Wannatong et al 2004], as in fig (3d).
4- With (0.25 DMF + 0.75 CL.F), we gain an media with (14.5 μS/cm) as electrical conductivity and (25.4 mN/m) as a surface tension, this lead to produce the branch microfibers with diameter (1530-3310 nm), we notice an increasing of microfibers diameter for increasing of boiling point of this media and some branches appear, because there is an instability jets through electrospinning process. As in fig (3e)
5- To improvement the microfibers diameter and morphology , we select the other ratio of solvent (0.50 DMF + 0.50 CL.F), this is represent the best ratio which leads to more controlling in microfibers diameter and morphologies. This media had (5.2 μS/cm) as electrical conductivity and (18.90 mN/m) as a surface tension. This media gives an microfibers with (390- 1060 nm) diameter.
   Increasing of electrical conductivity, decreasing of the surface tension, and suitable of the boiling point of media lead to higher affectivity of solution with applied electrical field and reducing of microfibers diameter. As in fig (3f)
   more controlling branches appears because there is an instability jets through electrospinning process. Finally, the addition of an organic solvent such as ethanol with little ratio (0.5 DMF+0.3 CL.F+0.2 Eth.) leads to decreeing of the microfibers diameter because it causes increasing of electrical conductivity of media solution up to (10.8 μS/cm) and decreasing of the surface tension up to (16.46 mN/m), with lower boiling points. [Wannatong *et. al*., 2004] as in fig (3g).

Conclude from the previous shapes (3a-g), the composition of the solvent media is a very important parameter for improvement of the resultant microfibers for this reason must the suitable solvent media depending on:

a. conformation of the dissolved polymer chains.
b. ease of charging the spinning jet: corresponding to the conductivity of the solvent media.
c. cohesion of the solution due to surface tension forces: it represents an combination between the polymer and solvent media, but for the same concentration of polymer this parameter controlled by changing of the solvent composition the viscosity also increases threefold at constant polymer concentration (DMF +THF).
d. rate of solidification of the jet on evaporation of the solvent: this corresponding to the boiling point and Vulnerability.

When the solvent contravenes the (a. point) & (d. point), this lead to a gelatin structure with not good microfibers such as in fig (3e).

fig (4 a-c) show the effect of injection rate on PS Microfibers diameter for concentration of 0.13 con. w/v, at different injection rates (1.3,1.5,1.7) ml/hr ,and other constant parameters that, we notice :

1- The diameter of PS Nano fibers increases with increasing of injection rate, then with decreasing the flow rate to more than recommended, polymer solution will get enough time to polarizing.
2- With very high flow rate thicker fiber diameter with formation of beads were produced, this due to the short drying time before arriving at collector and low stretching forces .

Fig (5), show the relationship between electrospinning distance and fiber diameter.

Fig (6 a-b) shows the effect of voltage type on morphology and diameter of PS/0.5 DMF+0.5 CL.F Microfibers I.R =1.5 ml/hr, N.D=0.89 mm, d=10 cm , AC-HVPS & DC-HVPS = 15 Kv, we notice:

1- The resulting Nano fibers with DC-HVPS more smooth and less beads than resulting Nano fibers with AC-HVPS, this because the AC – voltage has different values at each point which are non-symmetry. This leads to result the Nano fibers with irregular form with more beads at different shapes as in the previous forms , also there is an axisymmetric instability which happens with AC-HVPS, this leads to more beads.[Anthony ,2008] .
2- AC- HV lead to decrease of whipping process and increase of alignment of Nano fibers.[Anthony, 2008]

Conclusion :

1- increasing of voltage value, electrospinning, electrical conductivity lead to decreasing of Microfibers diameter but we notice appearing of some beads which controlling them by adding physical or chemical process.
2- Increasing of concentration, surface tension, viscosity, and flow rate leads to increasing of Microfibers diameter also with some beads which can control them by physical or chemical process.
3- DC-HVPS using leads to more smooth and thin fibers than AC-HVPS, but with lower alignment Microfibers.

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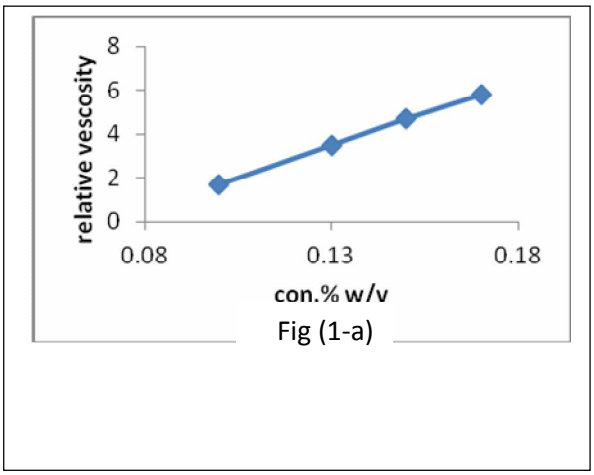


Fig (1-a)

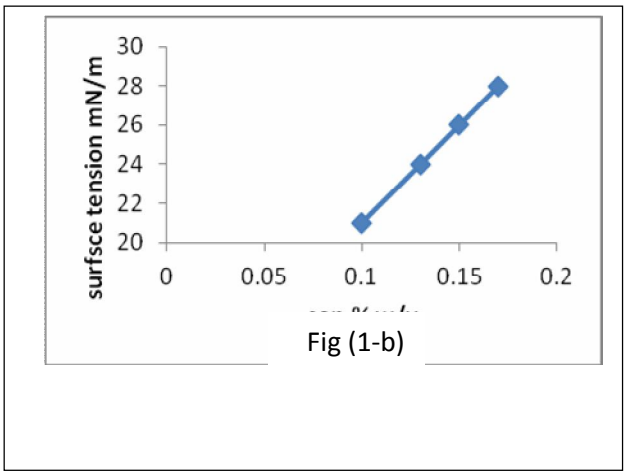
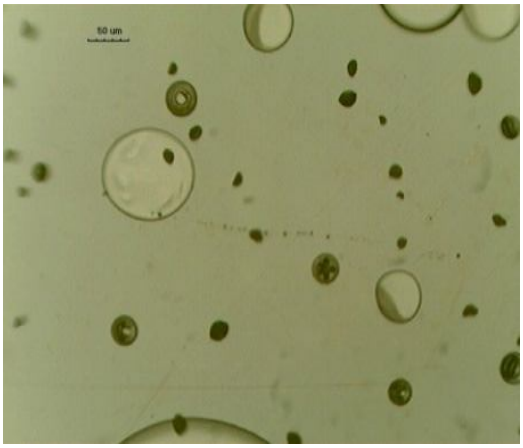
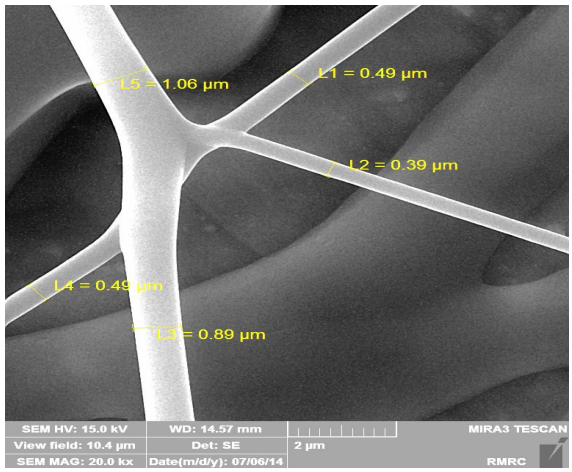


Fig (1-b)

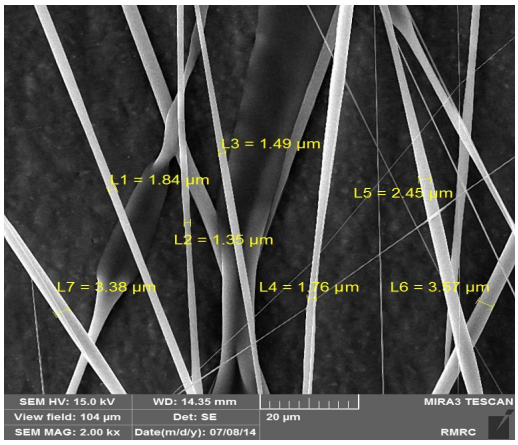
Fig. 1 a. the effect of con. wt. % on viscosity b- surface tension of PS/(0.5 DMF+0.5 CL.F) solutions



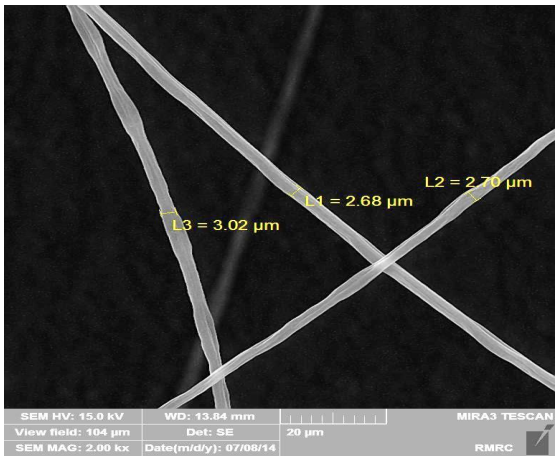
(a) critical con.%<<0.09



(b) 0.1% con w/v



(c) 0.13% con. w/v



(d) 0.15% con. w/v

Fig .(2 a-d) show the PS Microfibers at : AC- V=15 kV, I.R =1 ml/hr, N.D =0.89 mm, R.S = 360 RPM , d=7 cm, and different concentrations

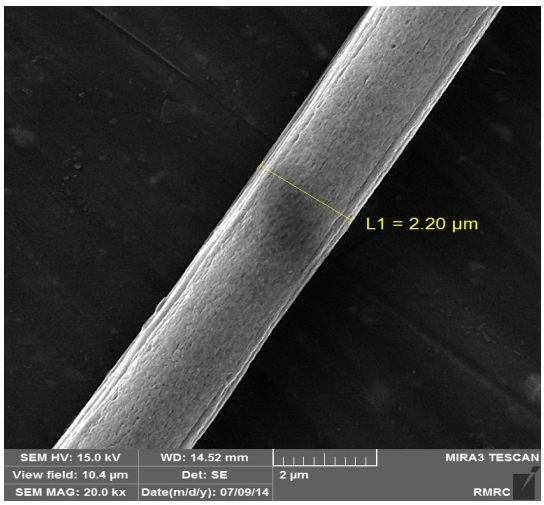


Fig (3.a) PS microfibers under DMF solvent

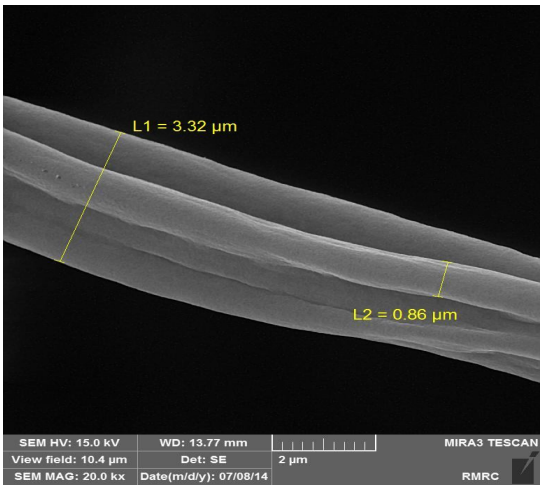


Fig (3.b) PS microfibers under THF solvent

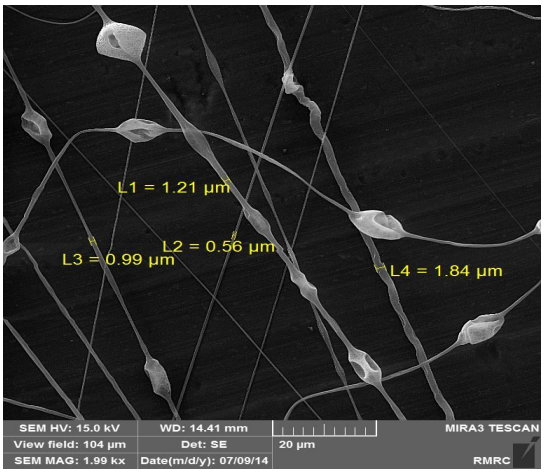


Fig (3.c) PS microfibers under DMF(0.25)+THF (0.75) solvent

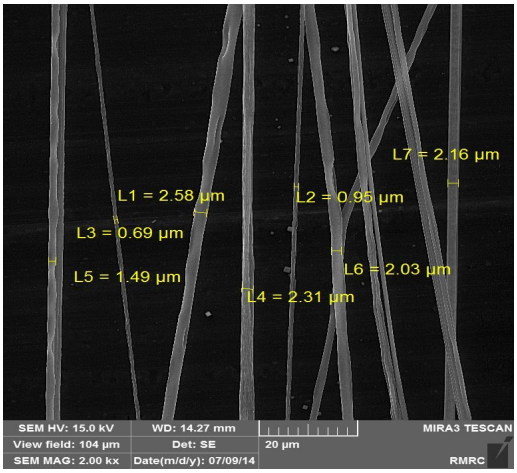


Fig (3.d) PS microfibers under DMF (0.25)+chloroform (0.75) solvent

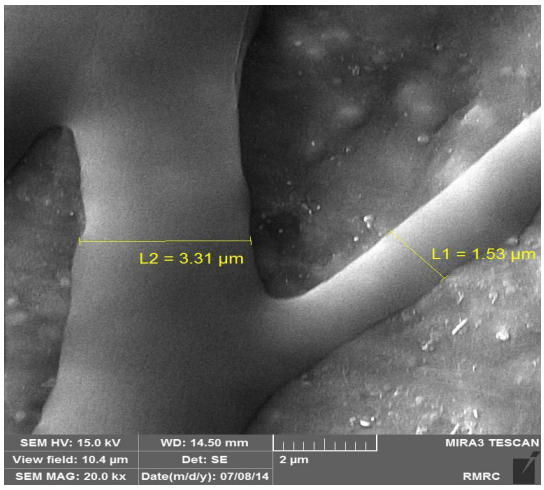


Fig (3.e) PS microfibers under DMF(0.75)+chloroform (0.25) solvent

Fig (2.b)

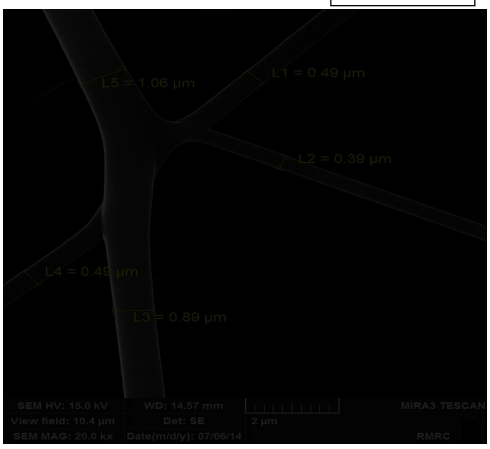


Fig (3.f) PS microfibers under (0.5) DMF + (0.5) CL.F solvent

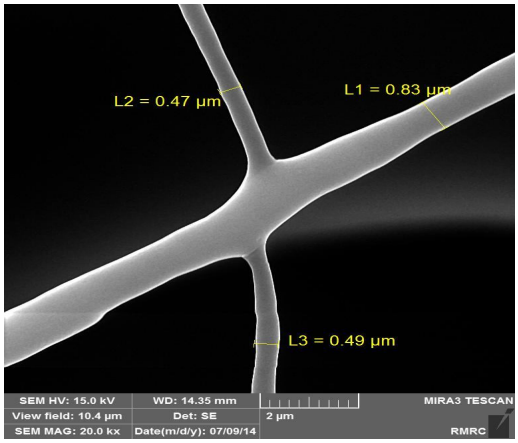


Fig (3.g) PS microfibers under DMF(0.5)+chloroform (0.3)+ethanol (0.2) solvent

Fig (3 a-g) PS Microfibers under 1 ml/hr I.R, , 360 rpm R.S, 15 kV-AC , 7 cm distance , N.D=0.89 mm, and con. w/v =0.1w/v and different solvent

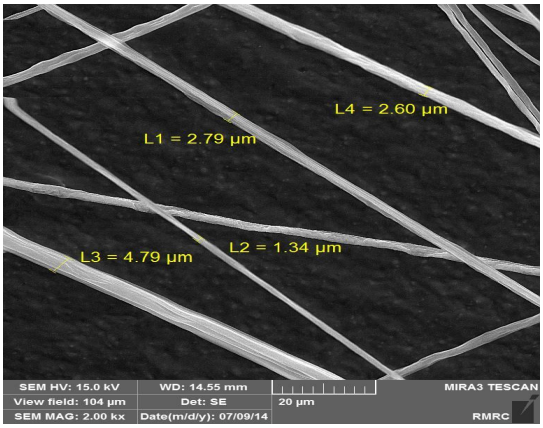


Fig (4.a) under 1.7 ml/hr I.R

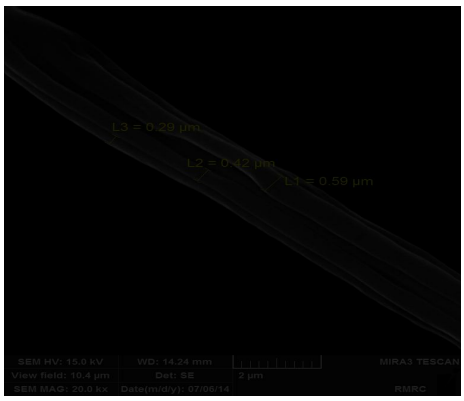


Fig (4.b) under 1.3 ml/hr I.R

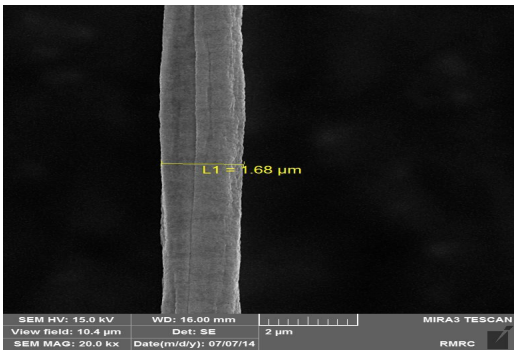


Fig (4.c) under 1 .5 ml/hr

Fig .(4 a-c) the PS Microfibers at : V=15 AC-kV, , N.D =0.89 mm, R.S = 360 RPM , d=10 cm, con.=0.13 w/v and different injection rates

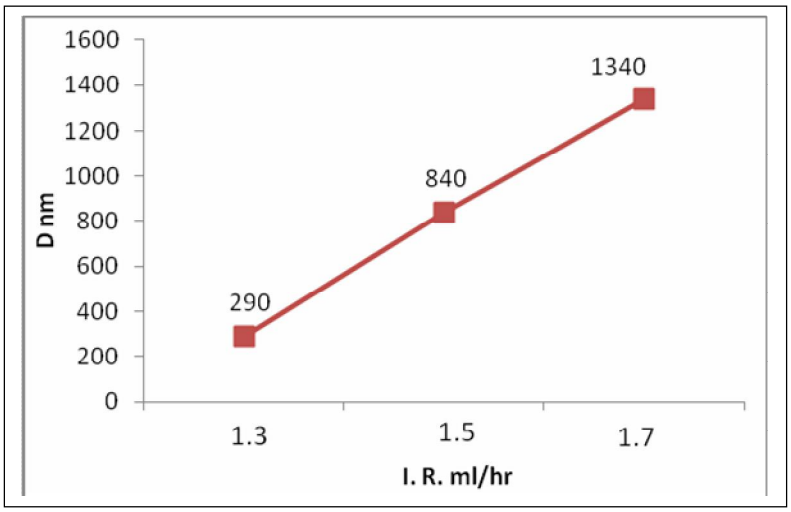


fig (5) the effect of injection rate on PS Microfibers diameter under : Needle diameter D =0.89mm, rotate speed = 360 RPM , distance between the tip of the needle and the collector d=10 cm, ,HV (AC) 15 kV & 0.13 con. w/v, and different injection rate I.R =1.7 , 1.5, & 1.3 ml/hr.

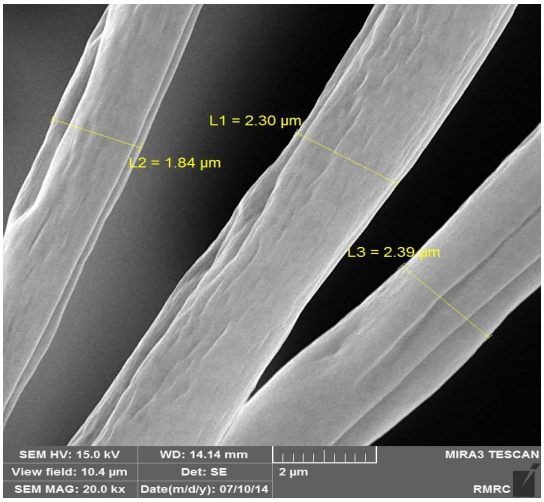


Fig (6.a)

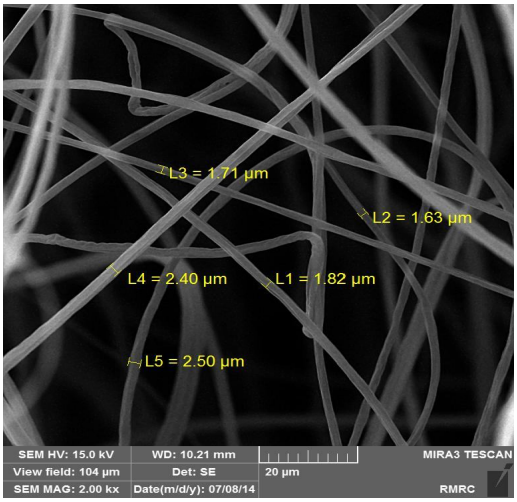


Fig (6.b)

Fig (6 a-b) show the PS Microfibers under (a) DC-HVPS = 15 kV (b) AC-HVPS 15 kV and I.R =1.5 ml/hr, N.D=0.89 mm, d=7 cm , con.= 0.15% w/v