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Investigation of biocompatible polymer poly(caprolactone)- chitosan as nanolayer contain vitamin E with two methods of electrospinning and finishing

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Abstract

One of the most necessary vitamins for human's body is vitamin E which many scientists investigated on release. In this study, two new compatible polymer (POLYCAPROLACTON and CHITOSAN) have used in the same time for creating a nano layer with this vitamin. Two methods of producing including electrospinning and finishing have studied. For this purpose, various percentages of polycaprolacton and chitosan have combined with vitamin E and produce with two methods. The surface morphology of nanofibers was studied by microscopy (SEM). By using infrared spectrometer (FTIR) the links between vitamin and nanofiber were studied. The effects of drug release and antimicrobial from nanofibers with standard (AATCC100) were measured. Based on the results of tests it was found that nanofiber PCL-chitosan containing vitamin with a ratio of 70-30 and a concentration of 1 gr and 0.3 gr that has produced with electrospinning, was shown the best speed and the best release in compared to concentrations and the other ratios and the speed of electrospinning was more than finishing and it had 81% Antimicrobial effects.

Keywords: Polymer, Nanofiber, Electrospinning, Drug Delivery, Vitamin E.

1. Introduction

Electrospinning is the best way for producing nanofiber and electrospinning is an interesting process for producing fine fibers with average diameters in sub micrometer down to nanometer range (around 100 nm).[9-14] In this process, a continuous string of a polymer liquid (i.e., solution or melt) was drawn through a spinneret by a high electrostatic force to deposit randomly on a plate named collector as a non-woven layer. [2-11] These fibers show several amazing characteristics, for example, a high surface area to volume or mass ratio, a small inter-fiber pore size with high porosity, vast possibilities, etc. [9]. These pros render electrospun polymeric fibers good candidates for a wide variety of applications, including wound dressing, medicine industry, filters [9-14], composite reinforcements, drug carriers, and tissue-engineered scaffolds [9-10].

Vitamin E was discovered in 1920. Vitamin E belongs to the group of fat-soluble vitamins and its chemical term is alpha-tocopherol. Vitamin E (tocopherols) is an indispensable vitamin for humans and animals. It is a well-known fat-soluble antioxidant. Since vitamin E decrease hazardous oxygen which is the cause of skin aging and offers a superior moisturizing effect, it is often applicable as a Medical industry functional cosmetics material. Furthermore, vitamin E has been widely used as a useful ingredient in drug medicine, food, etc. [7-8]. Whether taken orally or topically, studies indicated that vitamin E has antitumorigenic, photo protective, and skin barrier stabilizing properties, which makes vitamin E a commonly used for skin care products [9]. Usually, vitamins are practical to the skin in the kind of topical creams, lotions, or ointments. Vitamin E, also a fat- soluble vitamin, is known for its strong antioxidant ability, owing to the presence of a hydroxyl group on its chromanolring, which can easily donate a proton to fall free radicals (viz. free radicals can cause cell damage that may contribute to the development of heart and blood vessels disease and cancer) [5-9]. Therefore, there is a need for further research on vitamins and their release methods. Vitamin E is also one of the most useful vitamins for the skin of the breast, which can be prevented from breast cancer by the antioxidants present in it. [2-13] Many researchers investigated on vitamin E but they have not used two polymers(polycaprolactone) and chitosan yet. Also in this research used two methods including electrospinning and finishing

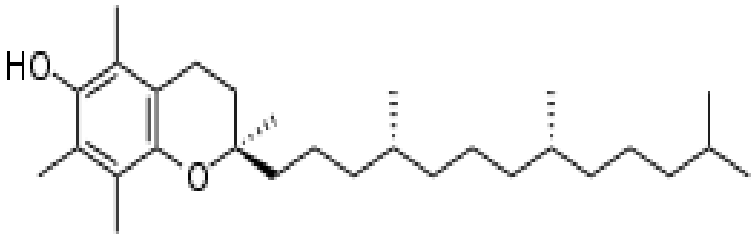


Figure 1. Structure of Vitamin E. [1]

There has also been researched in this area, for example, YutaYokozaki and his colleagues investigated on Loading of Vitamin E into silicone hydrogel by supercritical carbon dioxide impregnation toward the controlled release of timolol maleate. In this study, Vitamin E was loaded into the silicone hydrogel to decrease the diffusivity of timolol maleate. They resulted that the release system of timolol maleate in silicone hydrogel with the low diffusivity is created from the effective loading of vitamin into the silicone hydrogel by using the supercritical impregnation. [17] In another research, K. Son and his colleagues studied on fixation of vitamin E microcapsules on dyed cotton fabrics and they chose the pad-dry-cure method for this study. Based on the obtained their experimental results, they concluded that the fixation of vitamin E microcapsules on dyed cotton knit by pad-dry-cure method was very trustworthy in terms of durability of microcapsules and color fixity of the treated fabrics. [8]In third research, PallaviKamble, Bhakti Sadarani, and their colleagues studied on nanofiber based drug delivery systems for skin: A promising therapeutic approach nanofiber based drug delivery systems for skin: a promising therapeutic approach. Based on this argument, they talked about nanofiber and this review elaborates the advancements in the nanofiber- based mats in drug delivery for pharmaceutical and cosmetic use. [6-15] Due to the expansion of the new sciences in the various industries including nano technology and also according to the combining various sciences and finally, creating new technologies, there is a need to combine the medicine industry with textile industry. Also, the scientists received the best consumption with using nano sciences from these industries. So, the nanofiber is one of the best ways for combining these two industries that can carry the drugs and getting medicine to the body.[3-12] The drugs can be placed on the nanofiber with two ways (electrospining and finishing). So, there is a need to investigating these methods that which one is more cost effective and more efficient? On the other hand, the vitamins are of the necessities of the body that reduced in the human's body most of the times. [16-18] According to the vitamins can absorbed from the skin, different methods studied for vitamin release and various polymers used for this purpose. In this study, two new compatible polymers (polycaprolactone and chitosan) have used for carrying vitamin E and two methods of producing have selected (electrospining and finishing). At first, it has investigated that can these polymers carry vitamin E and at the second, which methods are more efficient?

2. Material and methods

Chitosan is the product of Sigma-Aldrich Company; poly caprolactone was produced from the laboratory Mehrazma, vitamin E was produced by Sigma-Aldrich, company and acetic acid 80% and 90%.

2.1. Electrospinning conditions

The voltage of electrospinning was 18.9 and a distance needle to the collector was 15 cm.

2.2. Analysis method

Chitosan was prepared at a concentration of 0.3 g and 0.5 g and PCL with two concentrations of 1g and 1.5 g. Both were prepared in a solution of acetic acid and were mixed together in the ratio of 30-70, 20-80, 50-50, 70-30, 80-20 and then is ready an electrospinning Table (1).

The electron microscopy (SEM) was used to identify the optimal sample of 20 samples. Fig (1) The infrared spectrometer (FTIR) was used For the detection of chain link, PCL-chitosan. Fig (3) Then were selected three examples of optimal concentrations of PCL-chitosan 80-20% and 1g-0.5g, PCL-chitosan 80-20% and 1g-0.3g, PCL-chitosan 70-30% and 1g-0.3g. The polymers were combined with vitamin E and were done electrospun again in another way,nanofibers were supplemented with vitamin E Table (2).

Table 1: samples without Vitamin E.

Materials and methods / Sample	Poly(caperolacton) 1gr	Poly(caperolacton) 1.5gr	Chitosan 0.3gr	Chitosan 0.5gr	Acetic acid (cc)	Distance needle to collector (cm)	Feed rate	Voltage (V)	Temperature °C
1	20%		80%		10	15	0.00	19.8	35
2	80%		20%		10	15	0.01	18.6	28
3	50%		50%		10	15	0.00	18.9	33
4	30%		70%		10	15	0.00	19.9	36
5	70%		30%		10	15	0.01	18.5	28
6		80%	20%		10	15	0.01	18.8	29
7		20%	80%		10	15	0.00	20.3	35
8		50%	50%		10	15	0.00	19.4	33
9		70%	30%		10	15	0.01	19.3	29
10		30%	70%		10	15	0.00	20.1	36
11	80%			20%	10	15	0.01	18.7	28
12	20%			80%	10	15	0.00	22.5	39
13	50%			50%	10	15	0.00	20.6	33
14	30%			70%	10	15	0.00	20.8	36
15	70%			30%	10	15	0.01	19.5	29
16		20%		80%	10	15	0.00	26.9	38
17		80%		20%	10	15	0.01	19.0	30
18		50%		50%	10	15	0.00	25.4	36
19		30%		70%	10	15	0.00	26.3	34
20		70%		30%	10	15	0.01	19.7	30

Table 2: samples with Vitamin E.

Materials and methods / Sample	Poly(caperolacton) 1gr	Poly(caperolacton) 1.5gr	Chitosan 0.3gr	Chitosan 0.5gr	Vitamin E (mg)	Aceticacid (cc)	Distance needle to collector (cm)	Voltage	Temperature (°C)
2	80%		20%		15	10	15	18.6	28
5	70%		30%		15	10	15	18.5	28
11	80%			20%	15	10	15	18.7	28

The electron microscopy was used for the detection sized of nano-fibers with vitamin Fig (2) and the infrared spectrometer was used to determine the link between vitamin and nanofiber. Fig (4) the antimicrobial tests with two Escherichia coli and Staphylococcus were performed with standard AATCC100. Fig (5) and the spectrophotometer was used to measurement drug release by using absorption, after drawing the standard graph of the vitamin in PH=5.5 and PH=7, in each sample, two parts were chosen and were placed into phosphate buffer with PH=5.5 and distilled water with PH=7. Then every 60 minutes was used spectrophotometer for write absorption and this practice has continued to until absorption zero. Fig (8) [11]

2.3. Tools spectrophotometer electron microscopy, infrared spectroscopy and absorption

Scanning electron micrographs were done by electron microscopy of MV2300 Camscan model at Tehran University, Faculty of Metallurgy and AIS 2300c Amirkabir University.

Infrared spectrometer of Model pectromone Manu factoring pekin Elmer Co was used for this study.

The tests of absorption were obtained by Cary 60 UV-Visible Spectrophotometer.

3. Results

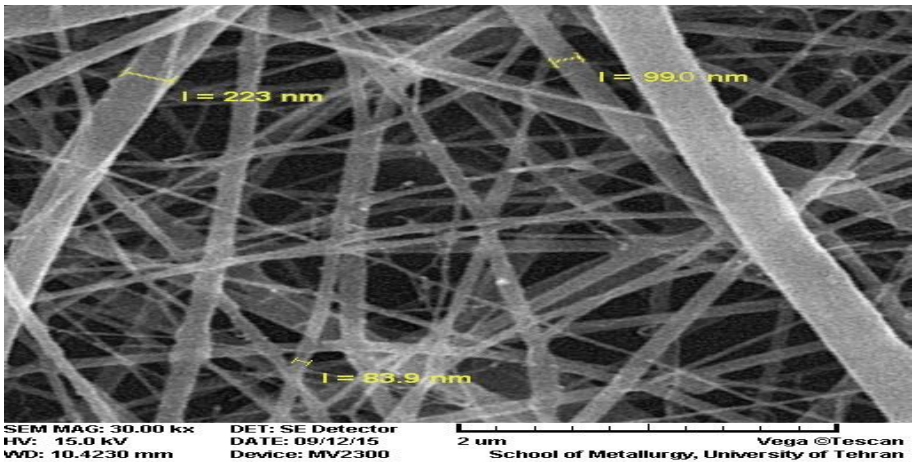
3.1. Scanning electron microscope test

PCL-Chitosan were mixed together with 20 different weight ratio. After the electrospinning, optimized samples were identified and selected by Using a scanning electron microscope (SEM). Fig (2) the average diameter of nanofibers was measured 84.86 nm. The samples S11, S5, S2 were selected as the best example. The samples were prepared again, this time with the vitamin was electrospun and in another way, nanofibers were supplemented with vitamin E, the photo of scanning electron microscope of nanofibers containing vitamin E have shown that increasing the diameter of nanofibers containing vitamin E. The mean diameter of nanofibers containing the medication is 159.5 nm and the photos of nanofibers have been supplemented with vitamin E, they have indicated the vitamin E sitting on the surface of the nanofibers and the vitamin has been linked with surface and if you enhance the resolution you can see the fibres under the vitamin. The methods were compared. Fig (3).

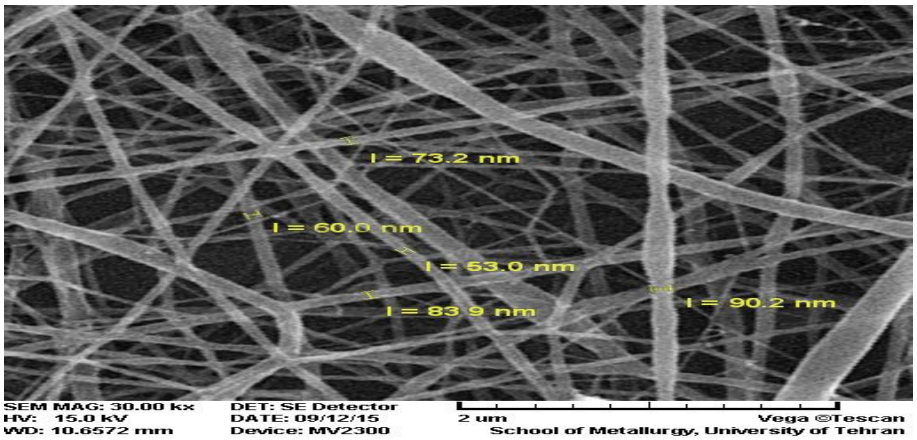
3.2. Infrared spectroscopy test

In FTIR, infrared spectroscopy of polycaprolactone, chitosan and nanofiber of polycaprolactone-chitosan are shown in Fig. (4). In chitosan, the broad peak at 3421 cm-1 was due to N–H and hydrogen bonded (O–H stretching). The peak at 2922 cm-1 was due to the asymmetric bending of C–H group. The N–H and –C–O–C peaks were observed at 1648 and 1100 cm-1, respectively. In PCL, the peaks at 2929 and 1729 cm-1 have represented the peaks for C–H and ester carbonyl groups. In PCL/CS scaffold, the O–H stretching has shifted to the lower frequency side and a sharp peak at 3437 cm-1 was observed. A slight bending at 1727 cm-1 is due to the presence of carbonyl group in PCL and another peak at 1166 cm-1 is due to C–O–C group.

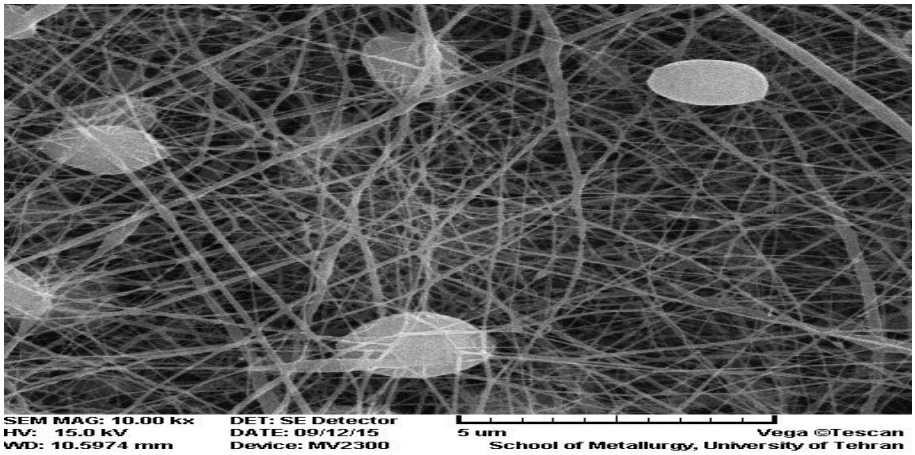
S18


l = 223 nm
l = 99.0 nm
l = 83.9 nm
SEM MAG: 30.00 kx
HV: 15.0 kV
WD: 10.4230 mm
DET: SE Detector
DATE: 09/12/15
Device: MV2300
2 um
Vega ©Tescan
School of Metallurgy, University of Tehran

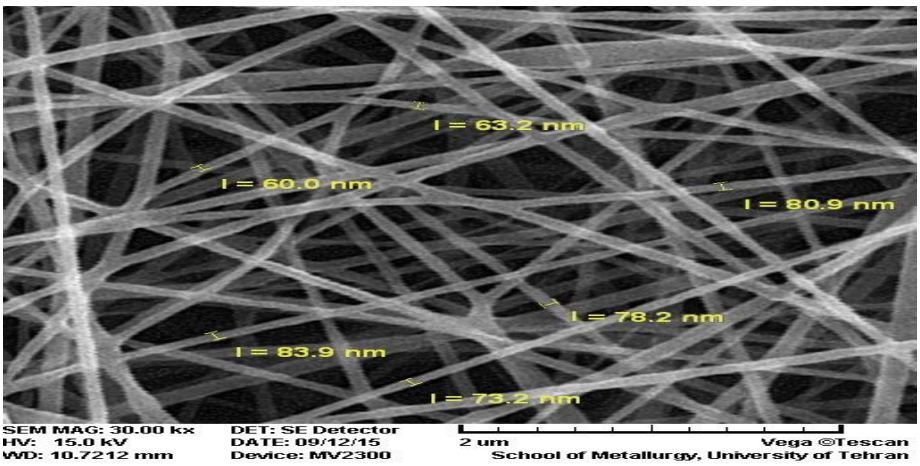
S11


l = 73.2 nm
l = 60.0 nm
l = 63.0 nm
l = 83.9 nm
l = 90.2 nm
SEM MAG: 30.00 kx
HV: 15.0 kV
WD: 10.6572 mm
DET: SE Detector
DATE: 09/12/15
Device: MV2300
2 um
Vega ©Tescan
School of Metallurgy, University of Tehran

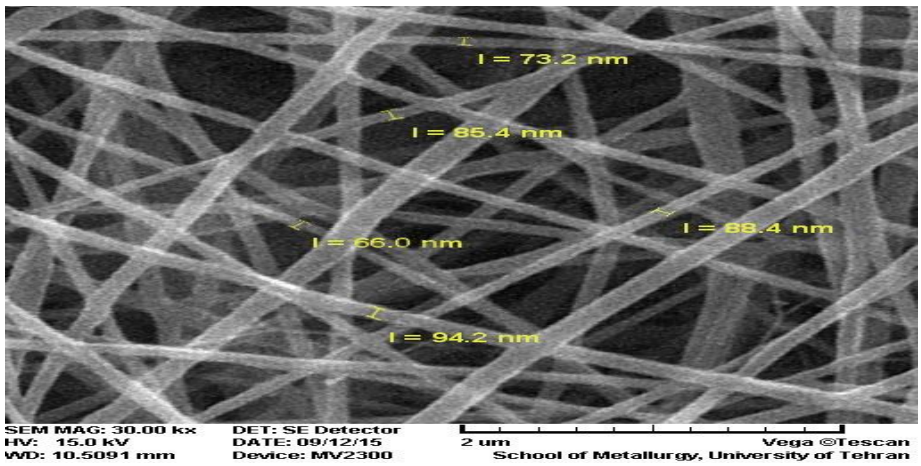
S7


SEM MAG: 10.00 kx
HV: 15.0 kV
WD: 10.5974 mm
DET: SE Detector
DATE: 09/12/15
Device: MV2300
5 um
Vega ©Tescan
School of Metallurgy, University of Tehran

S5



S2



S1

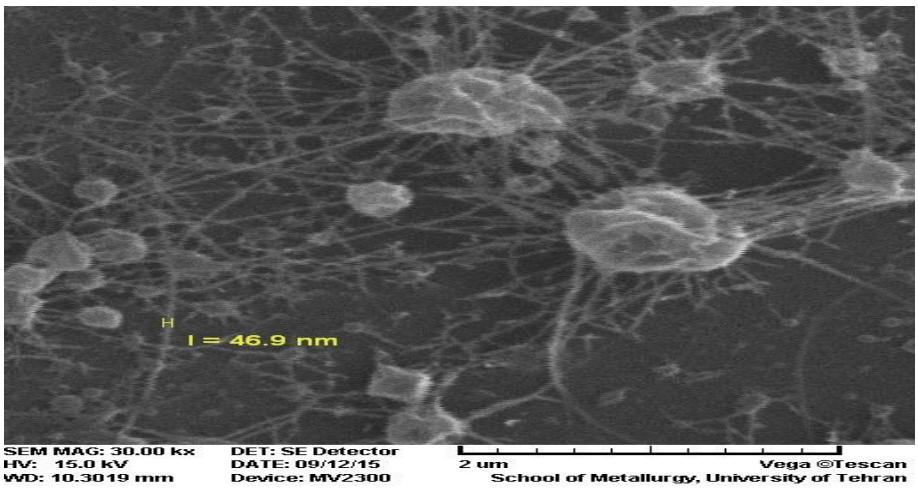


Figure 2. Scanning electron microscope image S18-50 % PCL 1.5 g, 50% CH 0.5 g S11- 80 % and 20 % PCL 1 g CH 0.5 g S7- 80% PCL 1.5 g, 20% CH 0.3 g S5- 70 % PCL 1 g and 30% CH 0.3 g S2- 80 % and 20 % PCL 1 g CH 0.3 g S13- 50 % and 50 % PCL 1g CH 0.5 g.

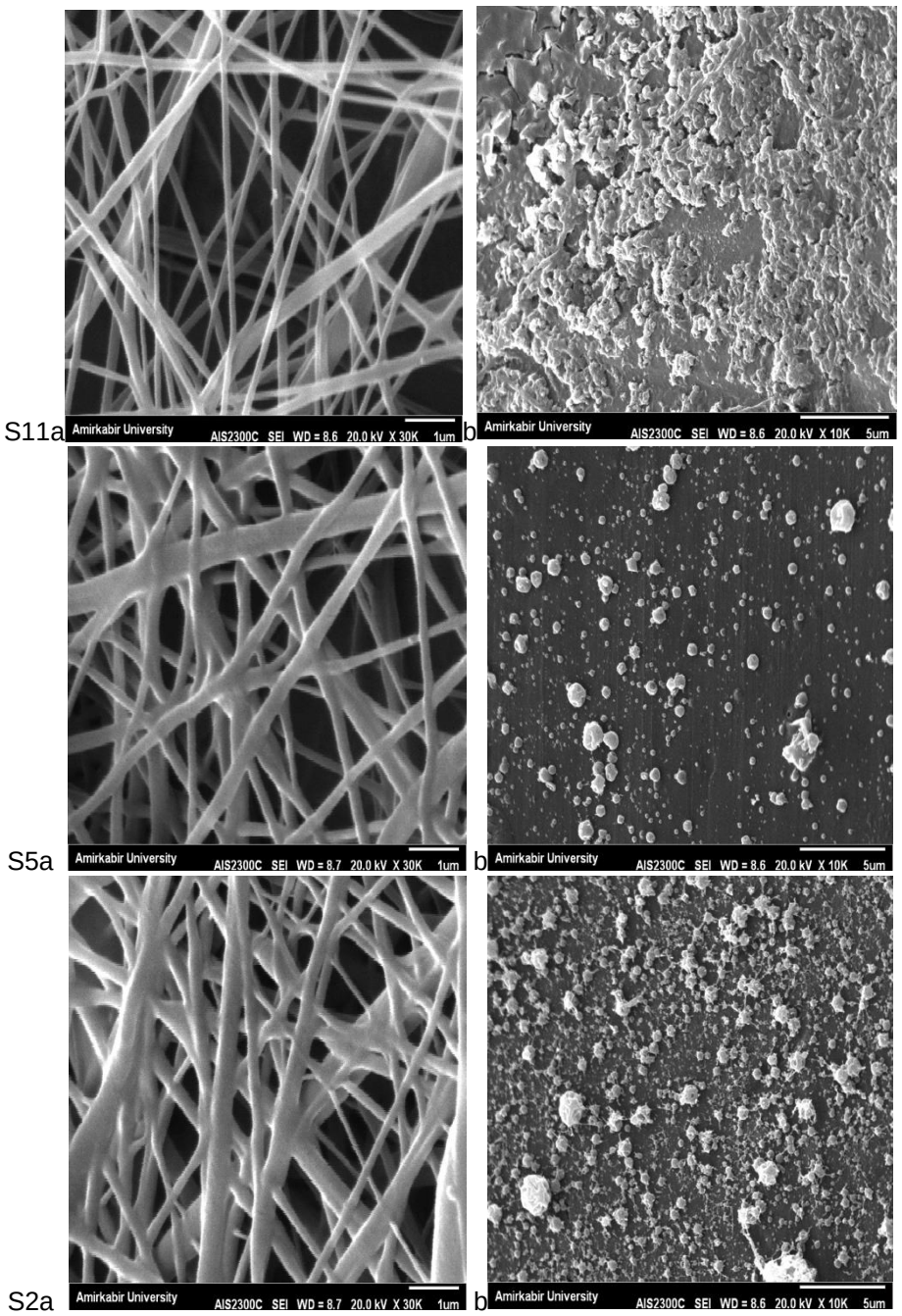


Figure 3. Scanning electron microscope image of nanofibers containing vitamin E a. electrospining polymer with vitamin E and b. supplement nanofiber with vitamin E.

From all these results, it is clear that the electrospun scaffold has contained both CS and PCL (Sarmila, Abhishek, Rajashree, Phani, &Nayak, 2009) [4]. New link areas 2944, 2869, 1727, and 1180 were indicated the presence of chains is due to polycaprolactone fig (4).The infrared spectroscopy has a wavelength of 2926-3435 that is due to the group CH and NH. The peaks in the 1619-1759 range and 1367-1462 range are due to CO groups and they related to the group -C = C- and CN and CH. The groups C = C is the 921-1078 range. By comparing the nanofibers containing vitamin E electrostatically generated and nanofiber supplemented with vitamin E

against nanofibers without vitamin can be realized to create weak links in the range of 3435 relating to the groups OH and NH 2948. It can be seen in the diagram one change with a very small slope in 1732 is related to - C = C- and another peak intensity of the C = C is in 1078 that can be accepted the link between vitamin and nanofibers but the links are very weak and they are van der Waals. However, according to the tests of spectrophotometers in drug delivery due to the good release and a top speed of it can be found that the links were established between the nanofibers and Vitamin E that they are weak and possibly the type of them are van der Waals and due to the presence of NH and OH It has also been hydrogen bonds, including bonds are weak, this interpretation establishes the link between vitamin E and nanofibers that are weak and can have a significant release fig (5)

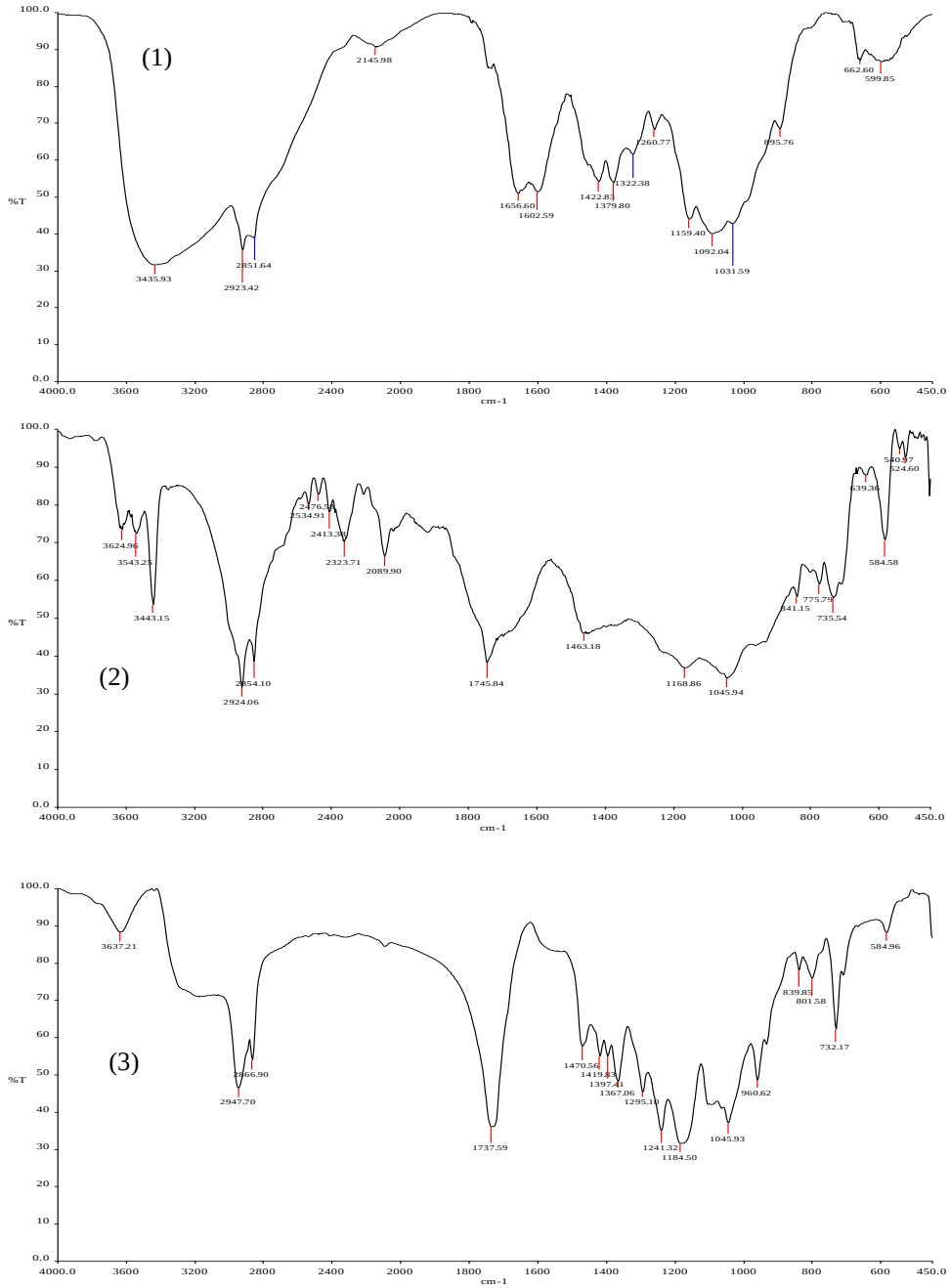


Fig (4). Infrared spectroscopy FTIR (1)- spectrometry infrared chitosan (2)- spectrometry infrared PCL (3)- PCL-chitosan nanofibres infrared spectroscopy.

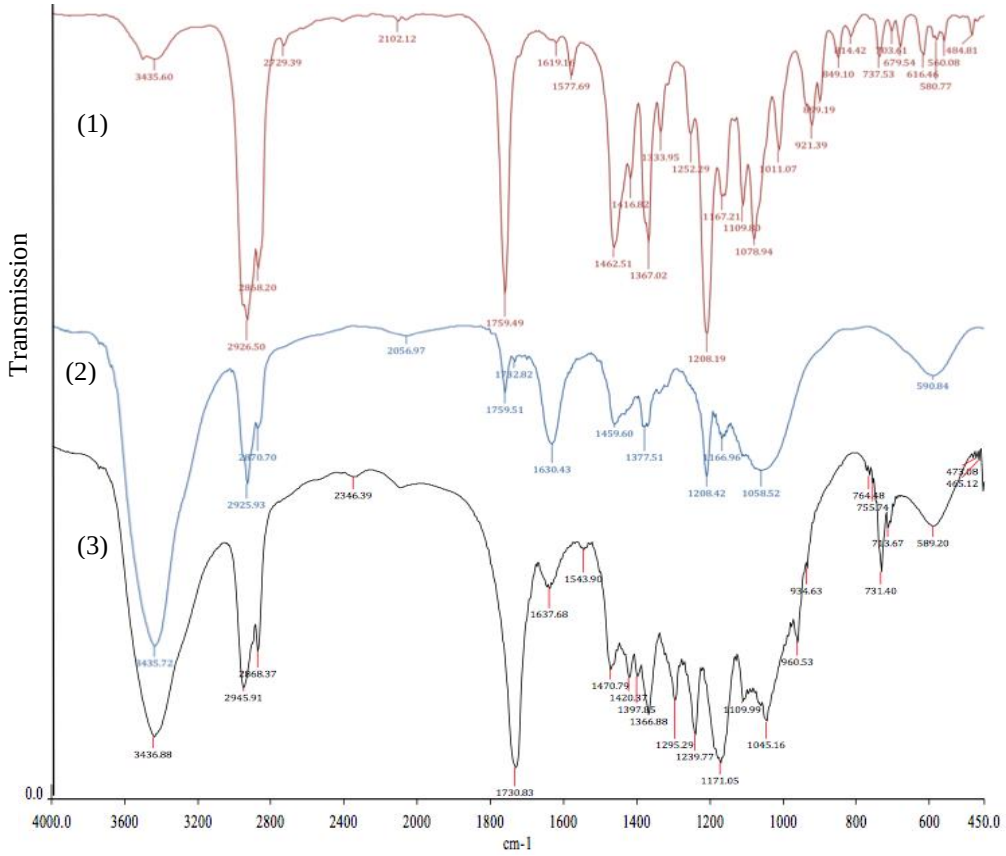


Figure 5. Infrared spectrometry 1- Infrared spectrometry vitamin E, 2- Supplement nanofiberwith vitamin E. 3- Electrospining polymer with vitamin E.

3.3. Antibacterial testing

Antibacterial testing of nanofibers containing vitamin was done on the bacteria Escherichia coli and Staphylococcus. The antimicrobial percentage was calculated according to the "Eq. (1)" And its results are shown in a graph Fig (6). Nanofibers containing vitamin E have shown better results in E. coli than nanofibers containing vitamin E in staphylococcus, As it can be seen in the graph in Figure 5 in E. coli 2.7% better treatment was shown than the Staphylococcus, and even in the nanofibers containing vitamin when PCL-Chitosan 80-20 volume percent when the PCL 1g and CH 0.5g are up to 83.12 percent have been treated against these bacteria and it's because of Concentration of chitosan. In the average, nanofiber with vitamin E against gram-positive and gram-negative bacteria, Escherichia coli and Staphylococcus have considerable influence along [19]

(Formula1: (a-b/b)*100) (1)

3.4. Drug release

The first graph is the standard graph of the vitamin in PH = 7 and PH = 5.5 that related to body and skin, they were drawn and find γmax after that two pieces of nanofibrescontaining with vitamin E were selected and they have been placed in PH = 7 and PH = 5.5. Then absorption numbers were measured every hour. It was continued until the vitamin E leave the fiber, in the early hours of his release drug has shown good and gradually it ended after 6 hours Fig (7).

According to numbers of absorption were obtained from absorption spectrophotometer and based on standard charts And charts were drawn from all three modes S11, S5, S2, it can be seen the release rate in S5 is more than two other and the highest amount of release is shown in both skin PH =5.5 and body with PH = 7. The test results of vitamin release were indicated a total release rate that was high Fig (8). Because link of chitosan and vitamin E with together, in a state S2, S11 are too weak and too strong, so in that case S5 has a good fit Fast and convenient delivery and high in total.The test result has shown the speed of release in aqueous PH = 5.5 is slower than phosphate buffer PH = 7 and the speed in nanofibers Was woven with vitamin E are faster than the nanofibers were supplemented with vitamin E and that's the reason

the first step is to remove vitamin has a longer interval. In comparison methods, the method (2) is faster than (1) and higher speeds have caused the release of high levels in the early hours but in the final hours of release is too low While the electrospun nanofibers with vitamin E (1) are slower and more appropriate time to release the vitamins. It can be said that this is due to vitamin sit on the surface of the nanofibersfibers supplemented with vitamins (No. 2) they enter easily and van der Waals bonds and hydrogen are broken and the vitamin releases.

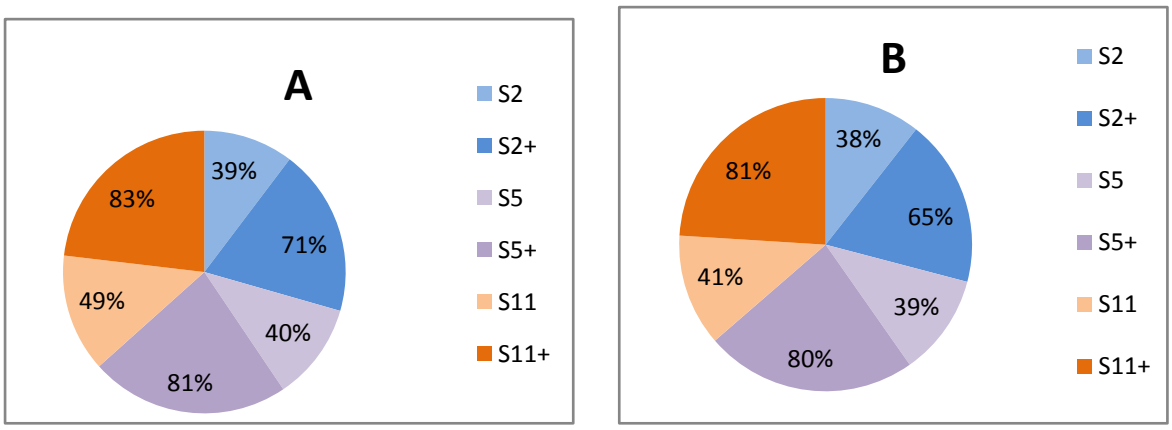


Figure 6. Antibacterial test A - E.coli and B- Staphylococcus

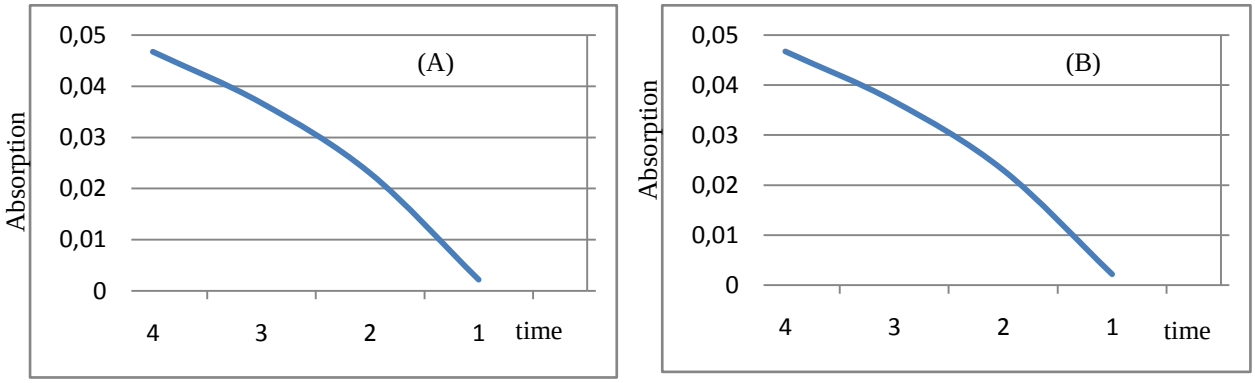


Figure 7. The standard graph drug. (A) . PH = 5.5 and (B) . PH = 7.

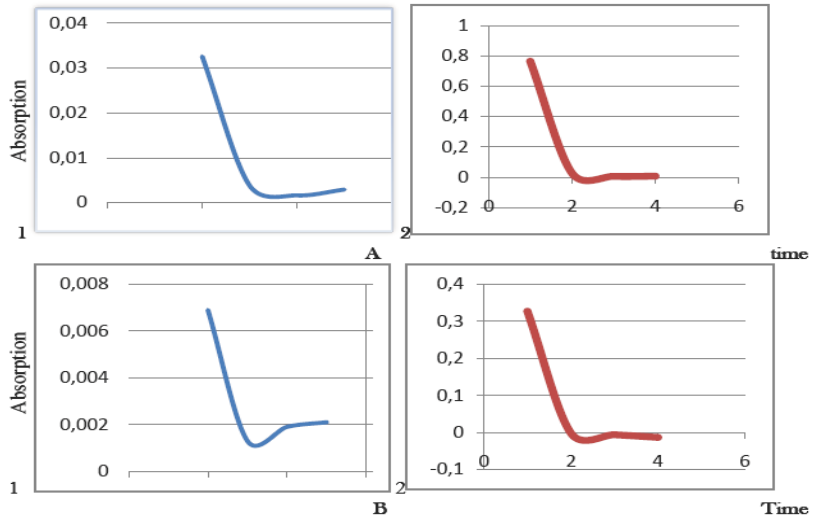


Fig (8). The graph of drug release from nanofibers made of PCL-Chitosan ratios 70-30 A- PH=5.5 and B-PH=7. Number 1.nanofiberselectrospun with vitamins and number 2. nanofibers supplemented with vitamins.

4. Conclusion

In this study, vitamin E was introduced with a new method of delivery. The photos of SEM were shown that the diameter of nanofibers has changed by adding vitamin E and shows it can be the impact of vitamins on the nanofibers. Results of infrared spectroscopy were confirmed PCL-chitosan nanofiber and were linked between vitamin with nanofibers and it was proved. Of course, this link is weak because of van der Waals link and exactly with this reason we've seen a good release, the links were created on the surface and they were just van der Waals and hydrogen bonds. Using antimicrobial testing has concluded that the nanofibers are containing vitamin with chitosan 0.5 g have antimicrobial percent more than other nanofibers with vitamins and it is because of chitosan, the concentration of chitosan was 0.5 and the antimicrobial properties were 83.12 percent. After conducting tests related to the delivery of vitamins, scaffold of nanofibers made of the PCL-chitosan optimal sample with the lowest concentration of chitosan with 70-30 as a superior carrier for vitamin E was selected. So it can show the maximum measure from their release at high speed. The tests result were indicated the slower release of Vitamin in aqueous (PH = 5.5) than phosphate buffer (PH = 7) and that's the reason, the first step is to remove vitamin has a longer interval and the release of vitamin due to enough time of phosphate buffer is more than aqueous. But in both, we had a high position in the speed and delivery. Finally, in this study was introduced 2 ways of putting vitamins on the fiber. They were electrospinning and finishing. So these ways can be used to bring vitamin to the skin or they can be used for preventing some cancer such as breast or skin cancer and even they can be used as a mask or wound dressing.

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