Abstract
Surface wettability plays a significant role in determining the function of the wound dressing. They should have hydrophobic surfaces for the adsorption of bacteria and a hydrophilic surface necessary to improve cell attachment for most anchorage-dependent cell types. Furthermore, the Hydrophobicity / Hydrophilicity of the surface can be used to direct cellular processes such as cell initial correlation, adhesion, and migration during wound healing, as a result such surface can change its surface wettability which increases the dressing's usefulness.

In this research, nanomembranes were prepared from polycaprolactone and chitosan solution (with different amounts of CS (0.05, 0.1, 0.2, and 0.4) % (w/w)) by the electrospinning method. These membranes were characterized by Fourier-transform infrared FTIR spectroscopy and their wettability, contact angle, porosity and swelling values were determined. These were improved by plasma treating the electrospun nanomembranes. Best results were obtained for the plasma treated electrospun nanomembranes at 4% chitosan. It resulted in a surface with a combination of hydrophobic and hydrophilic patterns, which has a lot of promise in the realm of tissue engineering for things like cell patterning and guiding.

Keywords: Polycaprolactone, chitosan, electrospun, plasma jet and wettability.
1. Introduction

The management of persistent wounds is a challenge problem because it impedes wound healing by containing malnutrition, illnesses (such as cancer and diabetes), and bacterial infection. Most of the presently utilized wound dressing materials suffer from serious drawbacks, such as mechanical and antibacterial characteristics. Wound dressings made from a combination of biopolymers like Polycaprolactone have several intriguing features, including high biocompatibility, enhanced biodegradation, good mechanical properties, antibacterial effects, and ability to stimulate tissue regeneration [1].

Chitosan (Cs) is a natural polymer produced by the deacetylation of chitin, a biodegradable polysaccharide polymeric source. Chitosan is suitable to the environment of tissue engineering, wound dressing, antibacterial, stem cell, electrospun nanofiber purification. Because of the time savings and inexpensive expenses, it has advantages to be used in the nanofibrous dressing [2].

These wound dressings are made using a cost-effective electrospinning technique that results in homogeneous also, continuous nanofibers with the formation of a porous structure with a high capacity of fibers and good swell ability, and ability to gas exchange, in addition to good cellular adhesion, and thus the good ability to provide moisture and heat, which ensures faster healing of wounds [3].

Wound dressings with better wettability and moisture retention are preferred for wound exudate management, others, on the other hand, are needed to help dry wounds retain moisture. The dressings must be of high mechanical strength to provide protection and adhesion to the wound. The materials used in the dressings are cellulose, chitosan, and collagen [4].

A specific change of the PCL surface is required for wound healing scaffolds made from electrospun Polycaprolactone (PCL) nanofibers [5]. Surface wettability is an important factor to considered when designing membranes for a variety of purposes, including anti-fouling surfaces, self-cleaning materials, and protective fabrics [6]. Plasma surface modification is a useful instrument for improving surface attributes without impacting a material's bulk properties. It may be used on any material to change mechanical properties, hydrophobicity, hydrophilicity, roughness, and surface chemistry in its most basic form [7]. Plasma activation adds a few groups of polar functions to the polymer surface, which improves wettability by increasing the polymer's surface free energy that helps cells function [8].

The fibrillary, porous structure of the electrospun Polycaprolactone (PCL) nanofibers is unfavorable to cell survival. To increase the bioavailability of Plasma treatment of polycaprolactone nanofibers, biomineralization of plasma coatings, and silk fibroin grafting [9].

Functional group formation, particularly radical-containing groups, makes it easier for plasma to change the surface chemistry of the polymer used. Non-polymerizing plasmas are commonly employed to alter the wettability of materials by adding a group of atoms
responsible for the characteristic reactions of a particular compound like (–COOH, OH), and (NH₂) [10].

Techniques such as XPS and FTIR, which detect variations in the community of chemical groups and states of the chemical bonding population, have been used to quantify the surface chemistry alterations of plasma-modified materials. Plasma treatment does not only present a change in free radicals, but there are functional groups that contain other functional groups such as carboxyl groups and aldehydes, C=O, NH₂, and fluorine, containing functional groups that depend on the type of gas used in the examination and the surrounding gas absorbed from the reaction of the roots with the gases to which the samples are exposed during the work that affects the surface [10, 11].

Nanofibers made of synthetic and natural polymers have been utilized as wound dressing materials. Because certain nanofibers are bioresorbable, they can be utilized as wound dressings which will be broken down by the body so, eliminating the need for removal of the dressing and the surgical and functional complications that come with it. Nanofibers can also act as a barrier between organs during the wound healing process, which is particularly important for severe wounds such as burns and chronic lesions such as ulcers [12]. Those nanofibers have been used as active wound dressing materials with the addition of bioactive species, and nanofibers are being intensively explored in the field of active tissue engineering with the inclusion of diverse bioactive cargos [13].

Zille et al. [14] have conducted a thorough examination of the use of the plasmas for textile alteration, mostly for non-medical purposes. They showed the effect of plasma on wettability for various polymeric fibers such as PE, PP, PET, polytetrafluoroethylene (PTFE), polyimide, polyamide, hemp, wool, aramid, leather, fibers of carbon and cellulose. Ferrero et al. [15] deal with the effect of a non-polymerizing RF air plasma on a cellulose film's wettability, adhesion, and coloring characteristics that are discussed. The wettability of several polar liquids was tested, and it was discovered that plasma treatment increased wettability.

Hodak et al. [16] found that the contact angle of the silk increased significantly when they used plasma in a hexafluoroethane atmosphere, and the energy of the surface decreased from the original value of 95-20 mg/m². The production of polar functional groups (usually –COOH or –C=O) that interact strongly with dipoles of surrounding water molecules is the basic functional mechanism driving plasma activation. These groups form in both oxygen-containing and inert gas plasmas (i.e., Ar, He, N₂) [17, 18].

2. Materials and Methods

Sigma-Aldrich supplied PCL with molecular weights ranging from 70,000 to 90,000. The solvent used was chloroform purchased from Aldrich (USA).

2.1 Preparation of samples

PCL was dissolved in chloroform at a temperature of 55°C and different concentrations of chitosan of (0.05, 0.1, 0.2, and 0.4)% were added. The solution was stirred for 3 hours at room temperature. Electrospinned Fibrous Scaffolding was prepared by expelling the prepared solution, using an infusion pump at a rate of 5 ml/h, from a syringe through an electric field towards an aluminum collector (Figure1). A 10 ml syringe with blunt-end needles of 18 and 22G was used. The needle tip distance from the aluminum collector was set to 10 cm. High voltage of 16–20 kV was applied between the needle and the aluminum collector. The
resultant nanofiber (Electrospined Fibrous Scaffolding) was dried overnight to reduce any solvent that remained on its surface.

![Figure 1: the electrospinning process](image1)

2.2 Surface Plasma Treatment

Plasmas (ionized gas) is used to alter the materials’ surfaces the use of nanotechnology in medical applications is fast advanced. The resultant fiber was dried overnight to reduce any solvent remained on its surface as shown in Figure 2.

![Figure 2: Plasma treatment on polymer surface [7]](image2)

The resultant electrospun nanofibers were plasma treated with diffuse coplanar surface barrier discharge (DCSBD) in argon gas flow at 1 atm. The DCSBD electrode system was created by screen-printing a pair of coplanar comb-like energizing electrodes with 1.5mm wide linear strips and 1mm lateral spacing on a 0.6mm thick 96 percent Al2O3 dielectric plate with a transformer oil insulated face Figure 3. A thin 0.3 mm layer of argon plasma spanning an area of 820 cm² was produced over the Al2O3 dielectric plate after energizing it with a 15 kHz sinusoidal high voltage at an input power of 90 W. A fine PET (Polyethylene
terephthalate) mesh was placed above the discharge electrode to hold the samples at a height of about 0.1 mm above the discharge electrode. All samples were treated for 3 minutes.

2.3 Fourier transformed infrared

FTIR spectrum analysis was performed in the range 4000-400 cm\(^{-1}\) utilizing a (Perkin-Elmer 2000) spectrometer with a resolution of (4cm\(^{-1}\)).

2.4 Field Emission Scanning Electron Microscope

A field emission scanning electron microscope (FESEM) was used to determine the shape of the nanofiber and to scan before cultivating cell lines. Surface roughness was measured at an operating voltage of 20-30 kV, and the roughness behavior was scanned using Gwyddion 2.45 softwareWhere: \((W_1)\) is the weight of a sample after alcohol immersion (gm), \((W_2)\) is the weight a sample before alcohol immersion gm, \(V_1\) is volume of the nanofibers (sample) which was calculated as \((V= length \times width \times thickness)\) before the immersion in ethanol (cm\(^3\)), and \(\rho\) = density of ethanol (gm/cm\(^3\)).

2.6 Swelling

Swelling test was carried out by soaking all samples in PBS (phosphate buffered saline) (pH = 5) at 37 \(^\circ\)C for 7 days. After gently tapping the nano fiber membrane using filter paper to remove the water excess, the swelled sample weights were measured. Eq. (2) [20] was used to calculate water uptake:

\[
\text{Swelling (\% )} = \frac{(W_s - W_d)}{W_d} \times 100
\]

Where, \(W_d\) = Weight of polymer (initial) gm, \(W_s\) = weight of swollen polymer (final) gm

2.7 Contact angle and wettability

Contact angle instrument was used to determine the wettability by dropping deionized water onto sample nanofiber membrane and measure the contact angle five times at different locations of the membrane and the average value was calculated.

3. Results and Dissection

3.1 FTIR

The stretching vibrations of hydroxyls and amines are ascribed to the band in PCL/Chitosan. Figure 4 shows the FTIR spectra (in the range of 3700–3000 cm\(^{-1}\)) of the nanofibers before and after plasma treatment. Peaks at 2923 cm\(^{-1}\), 2877 cm\(^{-1}\), 1411 cm\(^{-1}\), 1324 cm\(^{-1}\), and 1251 cm\(^{-1}\) correspond to various CH\(_2\) group vibrations, with the peak at 1382 cm\(^{-1}\).
corresponding to CH₂ wagging. Peaks for chitosan in PCL polymer are found at 2942 cm⁻¹ (I) (asymmetric CH₂ stretching), 2868 cm⁻¹ (symmetric CH₂ stretching), 1723 cm⁻¹ (II) (carbonyl stretching), 1292 cm⁻¹ (C-O and C-C stretching), 1239 cm⁻¹ (asymmetric C-O-C stretching), 1161 cm⁻¹ (symmetric C-O-C stretching), 1586 cm⁻¹ (NH₂ stretch), 1372 cm⁻¹ (–C–O stretching of the main alcohol), 1586 cm⁻¹ (NH₂ stretch), 1586 cm⁻¹ (NH₂ stretch), 1586 cm⁻¹ (NH₂ stretch), and at 1586 cm⁻¹ (NH₂)

The aldehyde groups can be converted to carboxyl groups during plasma treatment, and the hydroxyl groups can be converted to aldehyde groups or even carboxyl groups. The oxidation is caused by argon plasma treatment, however, it is not selective. It is worth noting that after plasma treatment, the intensity of the bands at 1324 cm⁻¹ and 1380 cm⁻¹ (seen in Figure 4) increased, which could be due to chitosan degradation processes.

Figure 4: FTIR of the electrospun nanofiber PCL/Chitosan (before /after) plasma Jet at 0.4%

3.2 FESEM

FESEM images were used to determine the diameter of the electrospun nanofibers prepared from PCL/ (0.05% &0.4%) Cs, as shown in Figure 5. The average diameters were (195.72, 107.44) nm for 0.05% Cs and (162.04, 47.26) nm for 0.4%Cs respectively.
Figure 5: FESEM images of plasma treated electrospun nanofibers plasma jet of (0.05% and 0.4%) Cs.

3.3 Contact angle and wettability

The wettability of a material's surface has an impact on cell adhesion, proliferation, and differentiation. Membranes to be used as wound dressings should have a dense top layer that protects the wound from physical damage and infection, as well as a porous and hydrophilic inner layer that absorbs wound exudate and offers a three-dimensional design that promotes cell attachment and proliferation.

Hydrophilic materials can provide moist conditions that are helpful to the healing process. Moisture susceptibility, permeability to air and water, and antibacterial activity of wound-dressing materials have all been reported to be influenced by plasma surface treatments. Plasma treatment has shown that it is not an effective method for changing the outer surfaces of the bandage, but it provides and gives the possibility of injecting chemicals and cells to aid in the healing process.

Table 1: Contact angle of electrospun nanofibers (with different contents of chitosan) before &after plasma treatment.

| Samples       | CA left ° | CA right ° | Average before plasma treatment | CA left ° | CA right ° | Average after plasma treatment |
|---------------|-----------|------------|---------------------------------|-----------|------------|-------------------------------|
| PCL           | 90.45     | 89.97      | 90.21                           | 90.45     | 89.97      | 90.21                         |
| PCL/0.05% Cs  | 92.50     | 96.18      | 94.34                           | 94.55     | 91.66      | 93.10                         |
| PCL/0.1% Cs   | 90.77     | 90.94      | 90.85                           | 92.55     | 92.90      | 91.72                         |
| PCL/0.2% Cs   | 89.26     | 89.13      | 89.19                           | 84.44     | 85.17      | 84.80                         |
| PCL/0.4% Cs   | 85.45     | 85.69      | 85.57                           | 34.03     | 31.75      | 32.89                         |
Figure 6: Contact angle of electrospun nanofibers (with different contents of chitosan) before & after plasma treatment.

| Samples   | Before plasma jet | After plasma jet |
|-----------|-------------------|------------------|
| PCL       | ![Image](image1)  | ![Image](image2) |
| PCL/0.05% Cs | ![Image](image3) | ![Image](image4) |
| PCL/0.1% Cs  | ![Image](image5) | ![Image](image6) |
| PCL/0.2% Cs  | ![Image](image7) | ![Image](image8) |
| PCL/0.4% Cs  | ![Image](image9) | ![Image](image10) |

3.4 Porosity

The porosity of a material is critical in tissue engineering because it provides void areas for cell accommodation and movement. The results showed (Table 2) that PCL provides the lowest porosity (40%), which increased to 53% when it was treated with plasma, which is essential for avoiding microorganism penetration. The different concentrations of chitosan added to PCL increased the porosity (55% to 83%) which was increased further after plasma treatment (73% to 89%). The porosity of wound dressings aids in proper gas, nutrient, and fluid exchange, as well as medicament release. For effective wound healing process, a wound dressing porosity is important to encourage cell adhesion and proliferation in the wound site. Total porosity values should be within the range of 60–90 percent. The electrospun fibers produced in this work were of porosity within this desired range. Porosity should be
appropriate for providing a suitable pore structure for cell migration and nutrient exchange, which is dependent on wound characteristics and wound management goal.

**Table 2**: porosity of PCL/Chitosan before & after plasma treatment

| Samples            | Porosity % before plasma treatment | Porosity % after plasma treatment |
|--------------------|------------------------------------|----------------------------------|
| PCL                | 40                                 | 53                               |
| PCL / 0.05% Cs     | 55                                 | 73                               |
| PCL / 0.1% Cs      | 61                                 | 81                               |
| PCL / 0.2% Cs      | 76                                 | 84                               |
| PCL / 0.4% Cs      | 83                                 | 89                               |

3.5 Swelling

Evaluation of the electrospun nanomembrane swelling profile is critical for assessing the membranes’ ability to absorb wound exudate. At defined time intervals, The end result is a PBS solution and their weight were observed. Based on the findings, the electrospun nanomembrane before plasma treatment displayed a high water absorption ratio increasing from (5.4 to 18.7). The plasma treated nanomembrane improved from (6.7 to 26.9) (Table 3). The hydrophilic elements in its composition of explains this finding. This result is very important because the nanomembranes’ swelling profile is consistent with the evacuation of excess exudate from the wound, which is generally produced during the inflammatory phase of the healing process (1–3 days after the damage occurs). In addition, chitosan possessed a high degree of swelling that was unaffected by the addition of the carboxyl groups that appear in Figure 4.

**Table 3**: Swelling of electrospun nanomembrane (with different contents of chitosan) before & after plasma treatment

| Samples            | Swelling % before plasma jet | Swelling % after plasma jet |
|--------------------|-----------------------------|-----------------------------|
| PCL                | 5.4                         | 6.7                         |
| PCL / 0.05% Cs     | 6.5                         | 8.9                         |
| PCL / 0.1% Cs      | 9.1                         | 12.8                        |
| PCL / 0.2% Cs      | 11.3                        | 18.3                        |
| PCL / 0.4% Cs      | 18.7                        | 26.9                        |

3 Conclusion

In this study, best results for wettability, porosity, swelling of the electrospun PCL/CS nanofibers (with different amounts of CS (0.05, 0.1, 0.2, and 0.4) % (w/w) based on the weight of PCL), were obtained at 4% CS which were greatly improved after plasma treatment. The values were of 32º, 89%, 26.9%, respectively. The findings revealed that these electrospun nanofibers had surfaces with moderate wettability allowing enough hydration at the wound site, improving fibroblast attachment and proliferation, thus they are appropriate for wound dressing applications.

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ilk fibroin nanofibers.

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Mohsen and Ali

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