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Electro spinning of Polycaprolactone / Hydroxyapatite Composites in Wound Dressing Application

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Abstract

Polycaprolactone polymer is widely used in medical applications due to its biocompatibility. Electro spinning was used to create poly (ε- caprolactone) (PCL) nanocomposite fiber mats containing hydroxyapatite (HA) at concentrations ranging from 0.05 to 0.4% wt. The chemical properties of the fabricated bio composite fibers were evaluated using FTIR and morphologically using field-emission scanning-electron microscopy (FESEM), Porosity, contact angle, as well as mechanical testing(Young Modulus and Tensile strength) of the nanofibers were also studied. The FTIR results showed that all the bonds appeared for the pure PCL fiber and the PCL/HA nano fibers. The FESEM nano fiber showed that the fiber diameter increased from 54.13 to 155.79 (nm) at the HA values from (0.05 % and 1%wt.).
Porosity, wettability of (PCL/HA) composites has improved, and the contact angle has decreased from 103.59^{o} to 85.57^{o} for fibrous scaffolds. The inclusion of hydroxyapatite increased the tensile strength of nano fiber scaffolds, and the maximum tensile strength of 0.4% percent was about 0.127 MPa, with a lowering in elongation to 40%.

Article Info.

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Polycaprolactone, Hydroxyapatite, Electrospinning, porosity, wound dressing

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1. Introduction

The development of nanotechnology in the last 20 years has focused a lot of interest on the electro-spinning process. This technique is used to create polymer nano- and microfibers and is very important in the bio-medical sector because of its low cost, scalability, flexibility, and simplicity [1]. The four basic components of an electro-spinning apparatus are shown in Fig. 1. A high-powered source, a hydrodynamic syringe a solution-filled syringe needle, a fiber deposition collector, and a high voltage power supply. An electric field is created between the collector and the needle when the positive electrode of the power supply is connected to the needle and the negative electrode is connected to the collector [2].
The creation of a Taylor cone occurs when the repulsive charge overcomes surface tension. This causes the polymer solution to flow to the negative electrode, which acts as a collector, enabling fibers to form.

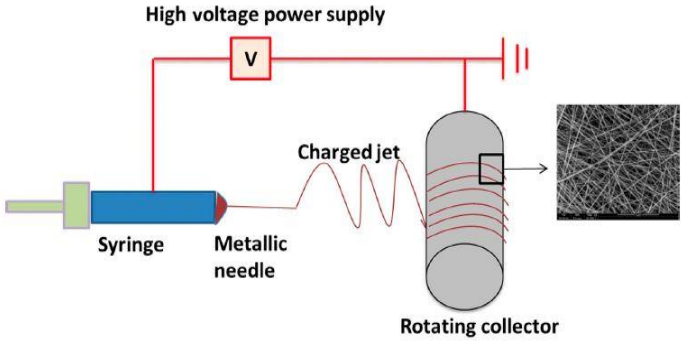


Figure 1: Electrospinning system with a rotating collector.

The polymer solution evaporates, and the dry fibers of the polymer solution are deposited on the collector in diameters ranging between nanometers and micrometers [3]. A number of factors control the electro-spinning process such as molecular weight, viscosity, solvents, surface tension, and conductivity/surface charge density. However, processing parameters such as voltage, collector/needle distance, flow rate, and syringe diameter, as well as environmental conditions such as temperature and humidity, play an important role in the production of nanofibers for electro-spinning [4, 5].

Polycaprolactone (PCL) is a synthetic polymer that is extensively used in the medical field, due to its biodegradation and biocompatible [6] and low melting point temperature of (55– 60) °C; PCL may be simply molded into the required scaffold design using various fabrication processes [7]. However, because PCL is hydrophobic, it lacks wettability and cell attachment when compared to hydrophilic materials. Its characteristics such as (bio-compatibility and delayed bio-degradation) and the quality of micro fiber structure created by electro-spinning could lead to a promising material for a range of applications, including medical [8]. For medical applications, PCL fiber must be nanofiber; this is crucial since fiber diameters must closely resemble natural extracellular forms in order to enable cell growth [9, 10].

Hydroxyapatite (HA) whose formula is a $[Ca_{10}(PO_4)_6(OH)_2]$ is one of the most vital materials for attraction due to its chemical similarity with the mineral part of the hard tissue bone is made up of two major components [11, 12]. Because of its biocompatibility, bio-activity, non-toxicity, osteoconductivity, and anti-inflammatory properties, HA has a wide range of biological uses and is osteoconductive, chemically, and thermally stable. However, due to its strong inclination to fracture as a ceramic, it has a weak tensile strength [13].

Mochane et al. [14] gave a mini-review on electron spun Polycaprolactone (PCL), one of the most often utilized synthetic polymers in medical applications due to its biocompatibility and delayed biodegradation. Combining the essential characteristics of the PCL matrix with the characteristics of nanofibers particles produces intriguing materials that might be used in a variety of applications, including biological ones. Nanofibrous structures have a huge surface area, a tiny diameter of pores, and a high porosity, all of which make them appealing for a variety of applications. For the creation of nano - and micro-sized fibers, electro spinning has been widely employed as a process. The many methods for electrospinning PCL and its composites to advanced applications are covered in this review. The steady-state conditions, as well as the influence of the membrane separation parameters on the electrospun fiber's shape, are also discussed.

Hassan and Sultana [15] electrospun bioactive nano-hydroxyapatite (nHA) into an electrospun Polycaprolactone (PCL) membrane to increase osteoconductivity or bone-bonding capabilities. The viscosity of PCL and nHA/PCL with various concentrations of

nHA, as well as the shape of the electrospun membranes, was evaluated using field emission scanning electron microscopy. The water contact angle of the nanofiber has been used to evaluate the wettability of membranes at various concentrations. Using atomic force microscopy, the surface roughness of electrospun nanofibers generated from pure PCL and nHA/PCL was measured and compared. The total reflectance has decreased. Using Fourier transform infrared spectroscopy, the chemical bonding of the composite electrospun nanofibers was examined. Beadle's nanofibers arose from the incorporation of nHA with a diameter of 200 - 700 nm. The fiber diameter and surface roughness of electrospun nanofibers were dramatically enhanced with the addition of nHA, according to the results. The water contact angle (132 ±3.5) for the PCL membrane was reduced after the addition of 10% (w/ w) nHA (112 ± 3.0). PCL membrane and 10% (w/w) nHA/PCL membrane ultimate tensile strengths were 25.02 2.3 and 18.5 4.4 MPa.

The major aims of this study were to create and characterize of PCL/HA nanofibrous scaffold for multifunctional wound dressing applications.

2. Experimental work

2.1. Materials and Methods

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

2.2. Preparation of samples

PCL was dissolved in chloroform solvent to prepare pure PCL at 55ºC. PCL/HA was prepared at concentrations of (0.05, 0.1, 0.2, and 0.4 %) the solution at 60°C for 3 hours until it becomes viscous. To synthesize the fibrous scaffold electro-spinning method by the prepared solution was pulled into a 10mL syringe with blunt-end needles of 18 and 22G. The needle tip's- aluminum collector distance was set at 10 cm. The needle was subjected to a high voltage of 16-20 kV. The solution was expelled using an infusion pump at a rate of (5mL/h). The resultant fiber was dried overnight to reduce any solvent remaining on its surface.

Figure 2: The Sample of composites.

2.3 Characterization

2.3.1. FTIR

Fourier transformed infrared (FTIR) spectrum analysis was performed using a resolution of 4cm^{-1} in the range 4000-400 cm^{-1}.

2.3.2. FESEM

A field emission scanning electron microscope (FESEM) was used to study the shape of the nanofibrous scaffold and to scan the surface roughness at an operating voltage of (20-30) kV.

2.3.3. Porosity

The porosity of the produced nanofibers was evaluated by immersing them in 100% ethanol until they were saturated and weighing them before and after. Porosity was determined using the following equation (1) for the ASTM C-20 [16]:

$$P = \frac{W_2 - W_1}{\rho\ V_1} \times 100\% \qquad (1)$$

where W_1 and W_2 are the weights of the samples (scaffolds) before and after immersion in alcohol, respectively, V_1 is the volume of alcohol before immersion in alcohol, and $\rho$is the alcohol density.

2.3.4. Water contact angle

The wettability of the membrane was evaluated using a contact angle instrument by dropping deionized water onto the membrane and measuring the contact angle five times at different positions on the membrane, with the average value derived for the ASTM - D5946 standard [17].

2.3.5. Tensile Strength

Mechanical characteristics of PCL and PCL/HA nanofiber composites were evaluated with an Instron Mechanical Tester with a 10 N load cell and a cross-head speed of 1 mm/min. Rectangular specimens were with (5x9x30mm) dimensions with load cell at a cross-head speed of 10 mm/min for the ASTM D- 882 [18]. Hooke law governs the relationship between stress and tensile strain.

Stress (σ) is defined ‘’as the measurement of the total average forces (*F*) per unit area of a surface (A) “shown by the relation;

$$\sigma = F / A \qquad (2)$$

Strain (*ε*) “is the proportion of total deformation to the original dimension of the material body to which forces are applied.” which does the relation express:

$$\varepsilon = (L\text{-}L^{\circ})/L^{\circ} \qquad (3)$$

Where: *L, L_o* are the original (initial) length and the length after applying the force, respectively.

Young’s modulus is a variant of Hooke's law of elasticity, as illustrated by the following relationship.

$$E = \sigma / \varepsilon = \text{stress} / \text{strain} \qquad (4)$$

where E is (Young's Modulus) which is a measure of stiffness.

3. Results and Discussion

3.1. Fourier Transmission Infra-Red Spectroscopy (FTIR)

Fig. 3 shows the FTIR spectrum of the pure PCL nanofiber which exhibits the characteristic peaks for pure PCL, at approximately 2940 cm^{-1} indicating the bonds of CH_2 for asymmetric stretching, 2865 cm^{-1} for the bonds of CH_2 for symmetric stretching, 1733 cm^{-1} bonds for carbonyls bond stretching, 1127cm-1 bonds of C–O and, C–C stretching in the amorphous phase 1164 cm^{-1} for carbon-oxygen bond stretching and at 1242 cm^{-1}.

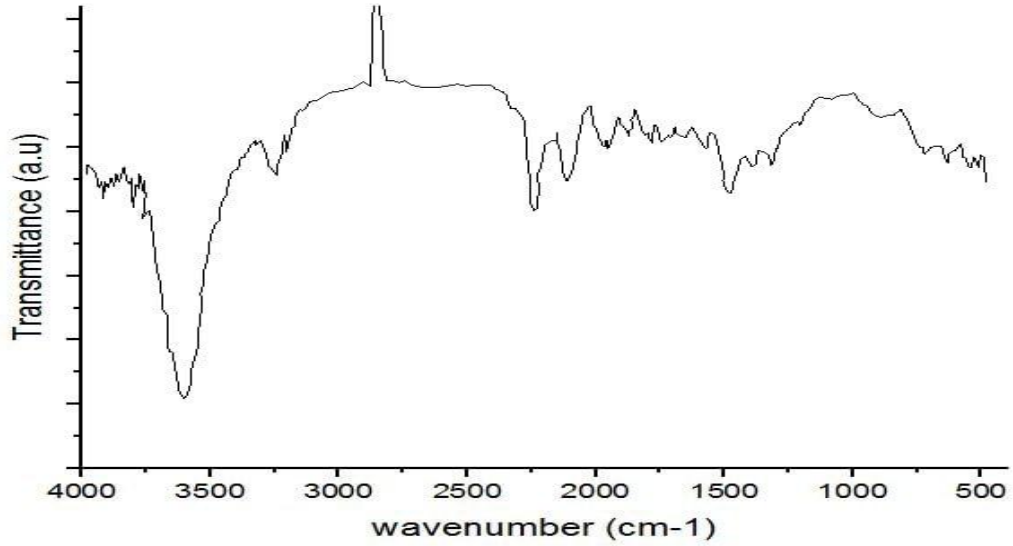


Figure 3: FTIR spectrum of PCL fiber.

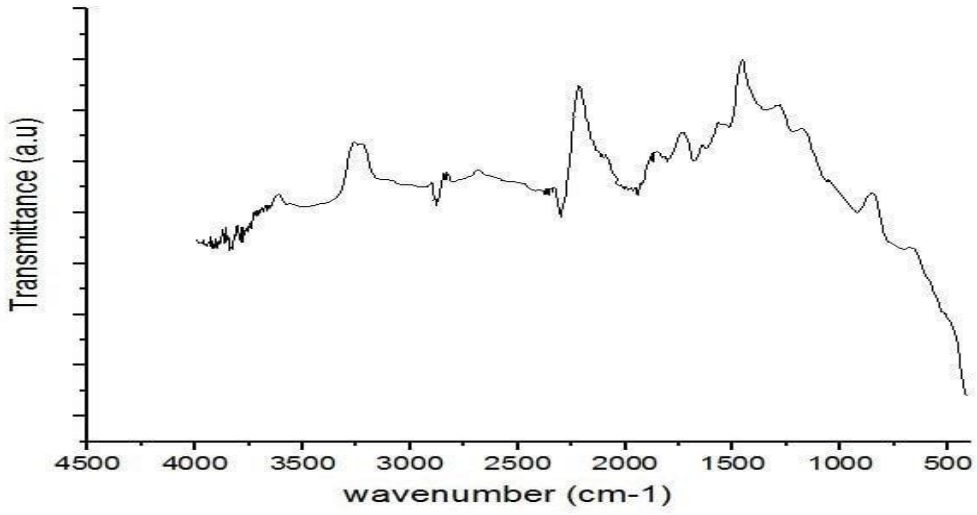


Figure 4: FTIR spectrum of PCL/HA fiber.

The FTIR spectrum of PCL/HA nanofibers is shown in Fig.4. It shows the peaks at 2923cm^{-1} for the bonds of asymmetric CH_2 stretching, the bond of 2884 cm^{-1} symmetric CH_2 stretching, 1720cm^{-1} for bonds of carbonyl stretching, and 1290cm^{-1} for bonds of C–O, and C–C stretching in the crystalline phase. PO4-3 absorption bands attributed to HA particles can be found in each of the HA and PCL/HA scaffolds, and at 499 and 1000 cm^{-1}, these $PO4^{-3}$ bands can be seen.

3.2. Field Emission Scanning Electron Microscopy (FESEM)

FESEM analysis was used to analyze the morphologies of the generated fiber. The pure PCL fiber exhibited smooth surfaces and a consistent fiber diameter distribution, as shown in Fig.5, with an average fiber diameter of around 52nm at different magnifications (1µm, 5µm, 200nm, and 500nm).

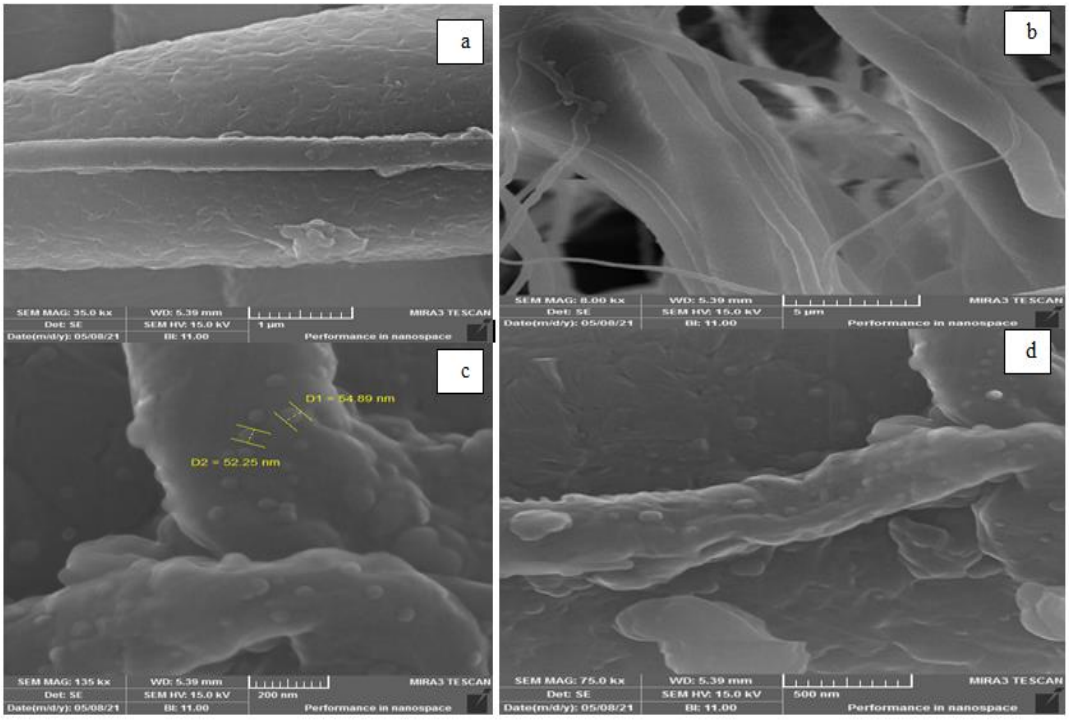


Figure 5: FESEM of pure fiber PCL at different magnifications a) 1µm, b) 5µm, c) 200nm, and d) 500nm.

The morphology and nanofiber diameter distributions for PCL/HA at (0.1 and 0.4%) are presented in Fig.5. The fibers were in wet form when reaching the collector during the electro-spinning process. According to Fig (6 and 7), the average fiber diameter increased with increasing the concentration of the polymer solution. At concentrations of 0.05%, and 0.4%, PCL/HA-based nanofibers diameters were 54.13 nm, and 155.79 nm, respectively. The smoothness of the surface can be attributed to the single phase of HA implanted through PCL fibers.

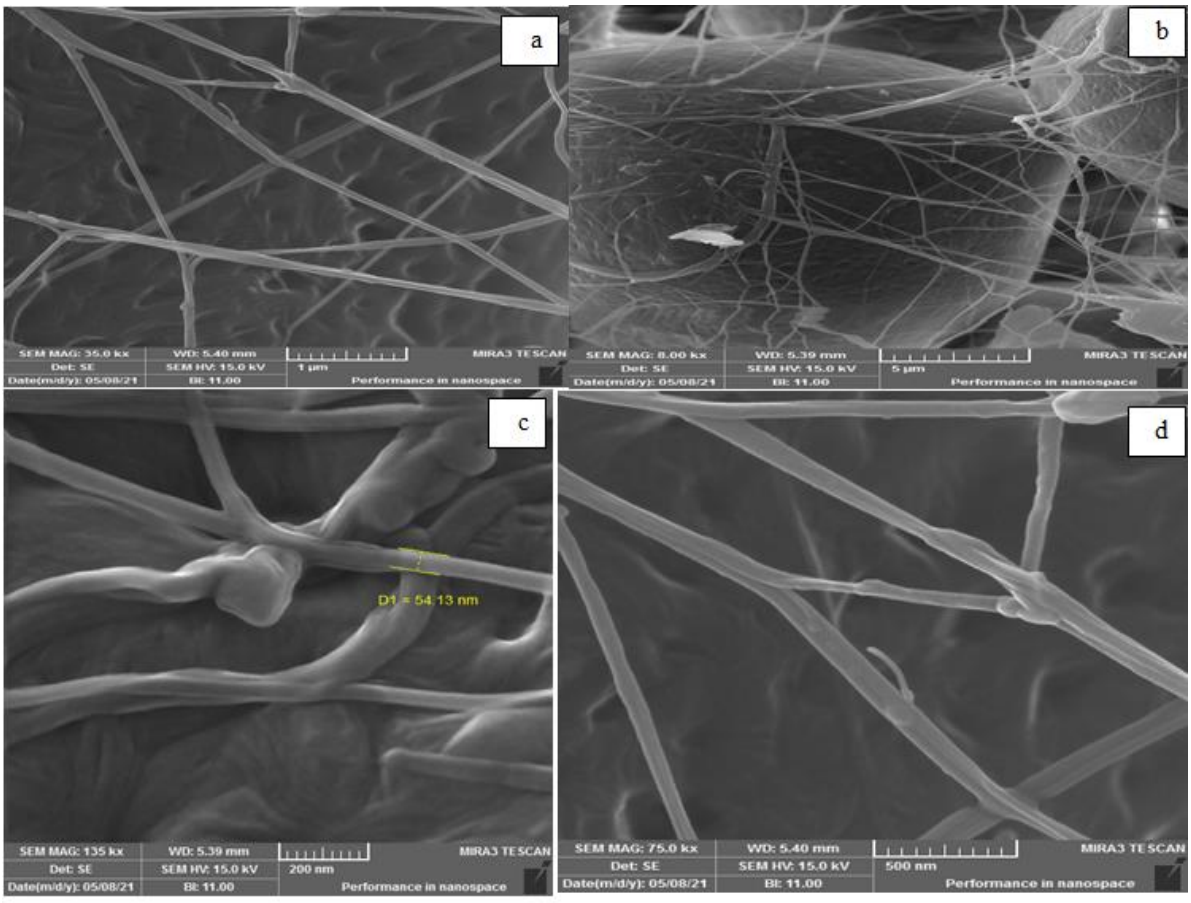


Figure 6: FESEM of PCL /HA 1/ 0.1 at different magnifications A) 1µm, b) 5µm, c) 200nm, and d) 500nm.

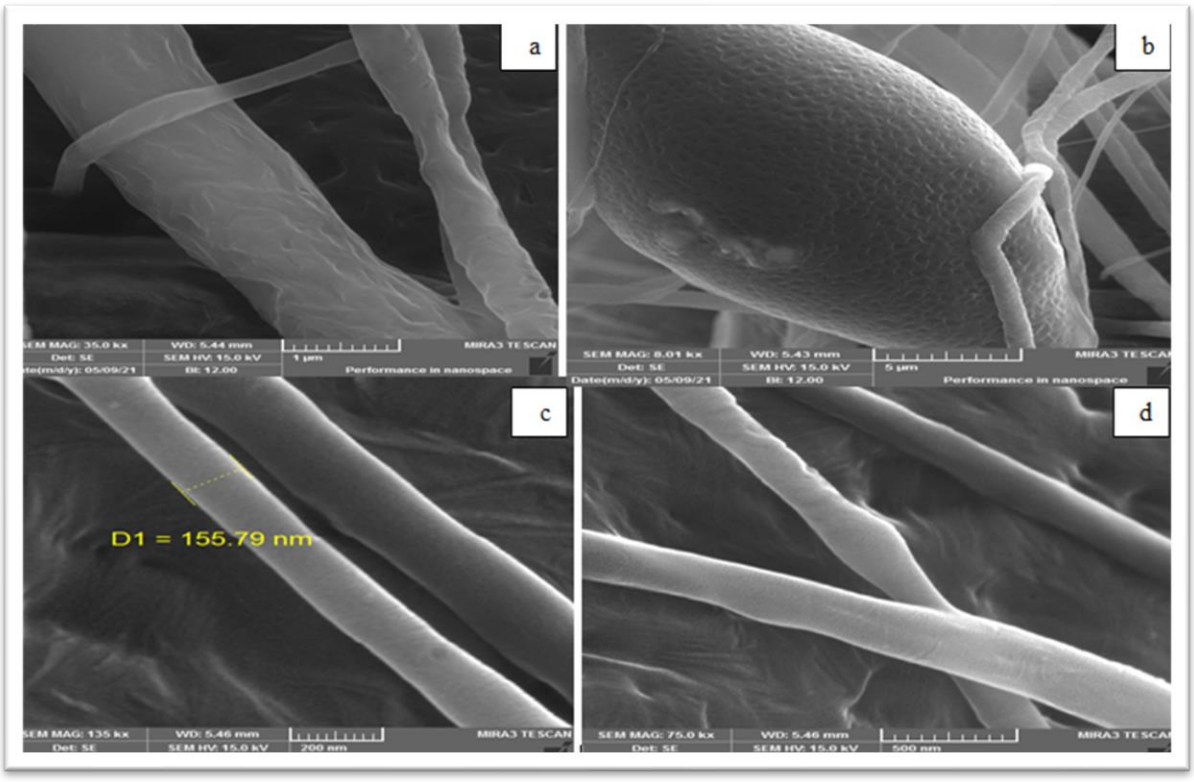


Figure 7: FESEM of PCL /HA 1/ 0.4 at different magnifications A) 1µm, b) 5µm, c) 200nm, and d) 500nm.

3.3. Porosity

The porosity of the nanofiber composites revealed that the porosity was high enough (>65%) in all produced nanofibres to be acceptable for wound dressing applications [19]. Table (1) shows that increasing the concentration of HA increased the porosity of PCL.

Table 1: Porosity of PCL/HA composites.

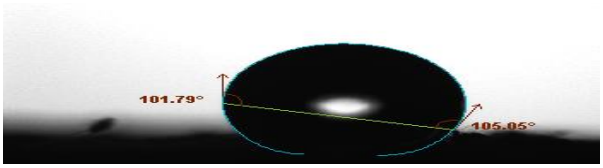
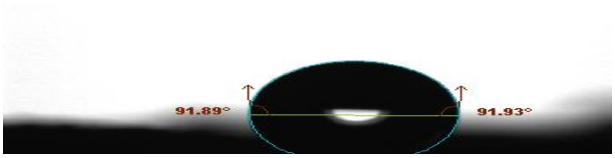
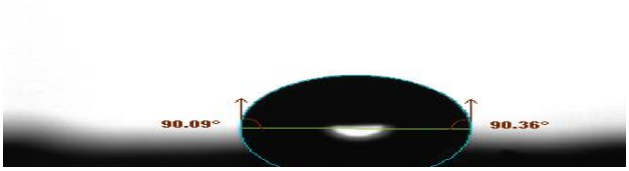
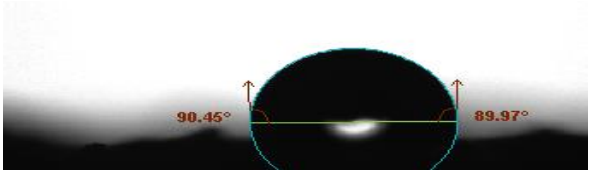
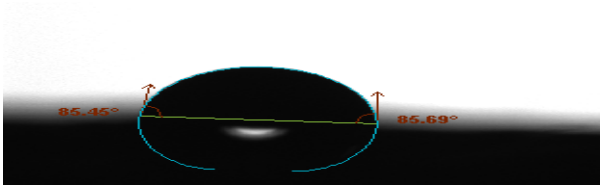
Sample	porosity%
PCL	**32.4**
PCL/HA 1/0.05	**51.5**
PCL/HA 1/0.1	**58.2**
PCL/HA 1/0.2	**71.3**
PCL/HA 1/0.4	**78.7**

When HA (with different concentrations) was added to the PCL sample, the porosity rose (between 51.5 and 78.7 %). The scaffolds' high porosity is advantageous as a wound dressing. Its function is not only for promoting hydration and preventing infection, but also for the transfer of nutrients and oxygen exchange [20].

3.4. Hydrophobicity and Contact Angle

From Table 2, it can benoticed that the PCL surface has a high value of contact angle around 103.59^{o} indicating the hydrophobic nature of the surface. As the HA content was increased from 0.05 to 0.4 percent, the wettability of PCL/HA composites improved and the contact angle falls from 91.91^{o} to 85.57^{o} respectively. A suitable wound dressing should be hydrophilic in order to absorb wound exudates while also keeping the wound bed wet. The hydrophobicity of the produced dressing was assessed using water contact angles, and the findings revealed that adding HA to PCL nanofibres decreased water contact angles. The chemical structure of HA and the nature of the hydrophilic OH group is responsible for the decreased water contact angle in PCL/HA nanofibers, in addition to the fact that hydroxyapatite is a hydrophilic material with a contact angle of about 10^{o} [21].

Table 2: Contact angles of PCL/HA composites.

Sample	Contact angle left °	Contact angle right °	Average	Picture
PCL	101.79	105.45	103.59	
PCL/HA 1/0.05	**91.89**	**91.93**	**91.91**	
PCL/HA 1/0.1	**90.09**	**90.36**	**90.22**	
PCL/HA 1/0.2	**90.45**	**89.97**	**90.21**	
PCL/HA 1/0.4	**85.45**	**85.69**	**85.57**	

3.5. Tensile strength

The mechanical characteristics of the dressing which is the most important component, influence its application because the tensile strength and flexibility of the dressing should be able to resist handling and replacement during the wound healing period. The ability of the nanofibrous scaffolds to be sustained under different applied stresses might introduce a high accurate evaluation of the fibers to be used or not clinical applications.

Fig.8 shows the ultimate tensile strength and Young's modulus of the electrospunned PCL and PCL/HA nanofibers calculated from the typical stress-strain curve. Young's modulus was calculated by Equation (4) which corresponds to tensile strength, Young's modulus increased from (0.0035 MPa to 0.1276 MPa), (2.01 MPa to 3.2 MPa), whereas elongation reduced from 155 % for the PCL specimens to 40 % as the HA content was increased from (0.05 wt. % to 0.4 wt. %). Mechanical properties, in general, can be altered

depending on composition. The tensile mechanical characteristics were also affected by porosity and fiber diameter. Both the modulus and ultimate tensile strength of electrospun PCL fibers in addition to the fiber distribution, and the good alignment improved the mechanical properties of the fiber. Thus, the FESEM micrographs exhibited higher tensile mechanical values and this agrees with the results of Johari et al. [22].

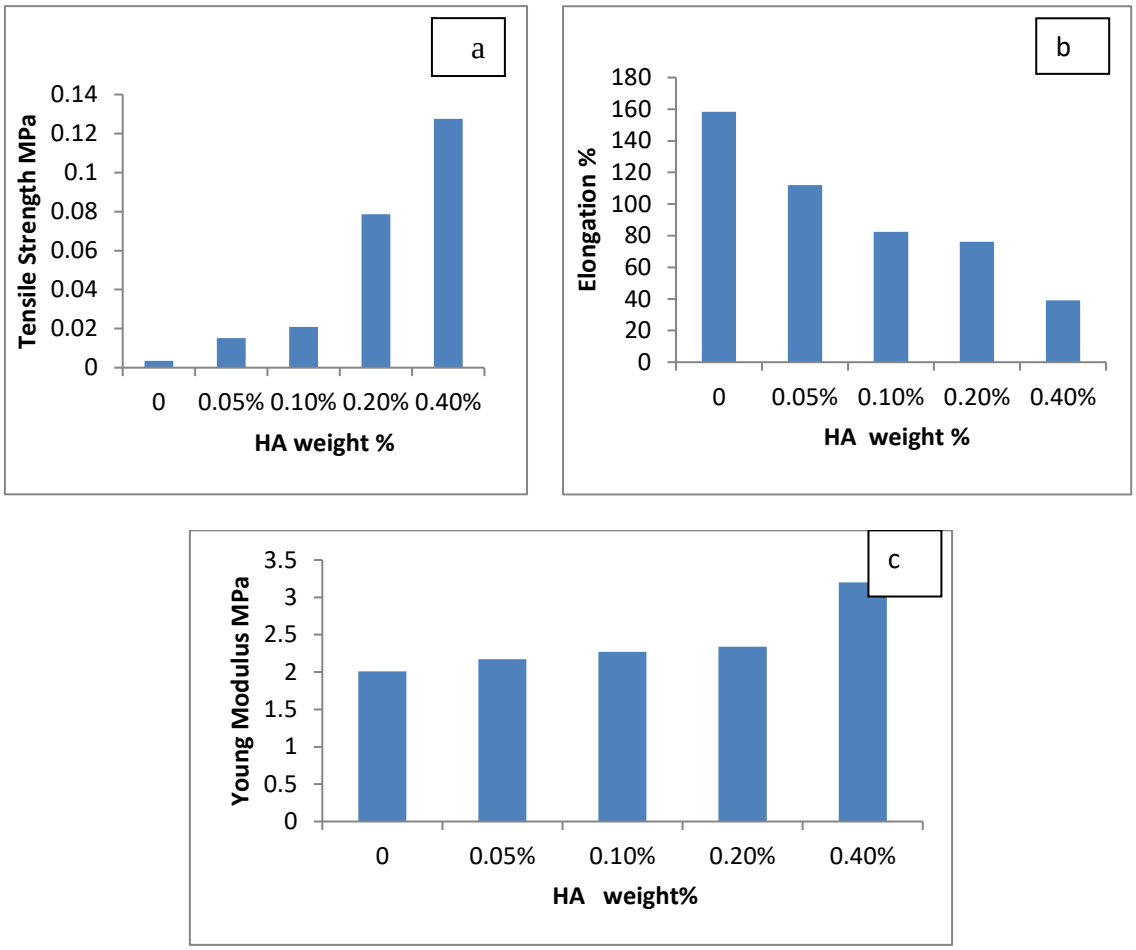


Figure 8: the mechanical properties of pure PCL and (0.05-0.4%) (PCL/HA) composite: a) The Tensile strength, (b) Elongation, and (c) Young modulus.

4. Conclusions

The results have shown that; the fiber diameter of PCL/HA, nanofibrous composites increased as the HA, concentration was increased, from 54.13 for PCL to 155.79 nm with 0.4% HA concentration (as revealed by the FESEM results), porosity increased from (51.5-78.7) %, wettability of PCL/HA, composites have improved and the contact angle decreases from 103.59º to 85.57º. The decrease of the contact angles may be attributed to the increase in porosity. The tensile strength of PCL/HA nanofibrous scaffolds was improved with the addition of hydroxyapatite and the maximum tensile strength at 0.4% HA was around 0.127 MPa while elongation decreased to 40% and Young modulus increased to 3.2 MPa.

Acknowledgments

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Conflict of interest

The authors declare that they have no conflict of interest.

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الغزل الكهربائي لمركبات البولي كابرولاكتون / هيدروكسيباتيت في تطبيقات ضماد الجروح

علي حسن محسن، نادية عباس علي
قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

بسبب التوافق الحيوي والتحلل الحيوي البطيء، يستخدم البوليمر الصناعي البولي كابرولاكتون على نطاق واسع في التطبيقات الطبية. تم استخدام طريقة الغزل الكهربائي لتكوين حصائر ألياف متناهية الصغر من البولي كابرولاكتون (PCL) تحتوي على هيدروكسيباتيت HA بتراكيزتتراوح من 0.05 إلى 0.4٪ بالوزن. تم تشخيص الألياف المتراكبة الحيوية المصنعة باستخدام FTIR وموروفولوجيه السطح باستخدام الفحص المجهري والمسح الإلكتروني (FESEM) والمسامية وزاوية التماس، وكذلك تم اجراء الفحوصات الميكانيكية (متانة الشد ومعامل يونك). أظهرت النتائج أن جميع الاواصر في FTIR ظهرت في ألياف PCL النقية والألياف النانوية PCL / HA المتراكبة .اما في فحص FESEM تبين ان قطر الألياف المتراكبة ازداد من 54.13 إلى 155.79 (نانومتر) عند القيم (0.05٪ و 1٪ بالوزن).

تحسنت المسامية بشكل عالي وكذلك قابلية التبلل لمتراكبات (PCL / HA) حيث انخفضت زاوية التماس من 103.59 إلى 85.57 للمتراكبات الليفية. أدى زيادة هيدروكسيباتيت إلى زيادة في قوة الشد لمتراكبات الألياف النانوية ، وكانت تم الحصول على أقصى مقاومة شد بنسبة 0.4% حوالي 0.127 ميكا باسكال، مع انخفاض في الاستطالة إلى 40٪.