Comparison of Mechanical Properties of Polyurethane Nanofilament Pulley with Natural Pulley as a Synthetic Structure
(A Cadaveric Study)

Abstract
Background: Pulley is a synovial tissue that attaches the flexor tendons to the dorsal portions of the fibro-osseous tunnel near the tendon attachment. Pulley type A with ring structure is one of the most important pulleys in fingers. Two-stage reconstruction by silicon is the common treatment in damaged tendon which has long recovery time and the tendency of the repaired tendon to adhere to the fibrous-bone tunnel around it. Accordingly, the one-stage reconstruction by synthetic pulley is a promising approach to resolve the mentioned problems.
Methods: In the present research, the polyurethane (PU) nanofiber scaffolds have been designed for synthetic pulley applications, and their mechanical and structural properties have been evaluated.
Results: The structural properties of nanofiber scaffolds show similar properties to protein and polysaccharide fibers in the extracellular matrix (ECM). The Fourier transform infrared spectroscopy (FTIR) results confirmed the functional groups of PU without any unwanted reactions. The amount of stress (3.19 ± 0.54) and Young's modulus (1.20 ± 0.39) in PU nanofiber scaffolds show similar mechanical properties to natural pulley.
Conclusion: The obtained results showed that the PU nanofibers scaffolds can be proposed as a suitable candidate for fabrication of synthetic pulley in flexor tendon injuries.
Keywords: Pulley, flexor tendon, Young's modulus, Nanofibers, Polyurethane

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Mehrnoush Nakhaei, PhD[1]; Nafiseh Jirofti, PhD[1]; Ali Moradi, MD[1]; Mohammad Hossein Ebrahimzadeh, MD[1]

[1]Department of Orthopaedics, Orthopaedic research center, Bone and Joint Laboratory, Ghaem Hospital, Mashhad University of Medical Science, Mashhad, Iran.

Corresponding author:
MH Ebrahimzadeh, MD
Email Address:
Ebrahimzadehmh@mums.ac.ir

Introduction

Pulleys are fibrosis bands segmentally positioned on the synovial sheath and stabilize tendons in the motion and rotation axes of the joints [(1)]. Pulleys are available in two variations, including; 1) type "A" pulleys, which are annular and amongst the most critical pulleys (especially types A2 and A4), and 2) type "C" pulleys, which are cruciate and less critical (than other pulleys). To have proper tendon functioning in the zone II flexor tendon, pulleys A2 and A4 should be healthy and operate efficiently [(2)].

The commonly used method to treat and heal a damaged tendon is a two-stage reconstruction. In this method, the tendons and tissues around the pulleys and pseudo- tendon sheath are first reconstructed using silicon Hunter rod implants. Then, the movement of the fingers is secured by support from the tendon graft in the motion direction. Following the formation of the synovium in the sheath, which takes two to three months, the silicon Hunter rod is removed and replaced with the tendon auto-graft. However, delayed flexor tendon system reconstruction is challenging for hand surgeons due to the long rehabilitation time and the tendency of the healing tendon to stick to the surrounding bone-fibber tunnel [(3, 4)]. In general, the two-stage tendon reconstruction has two drawbacks below:

1) The long period between the two stages takes two to three months.
2) The use of a tendon auto-graft to fabricate pulleys that causes damage to the donor zone.

Using synthetic pulleys for the delayed repair of tendon damages in one stage prevents the two-stage reconstruction of flexor tendons in zone I and II, which

usually involves two "pulley reconstruction" and "tendon auto-graft" stages and takes two to three months. This method provides the following benefits:
1) The need for one (instead of two) surgery.
2) The rehabilitation time is reduced by two to three months.
3) No need for tendon auto-graft for pulley reconstruction and thus no damage to the donor site; and
4) No need for silicon Hunter rod implants with their high costs and complications, and no fibrosis sticking of the tendon during tendon repair.
Given the above, the present study designs and fabricates synthetic pulleys with polyurethane (PU) nanofiber scaffolds to improve tendon functioning and diminish complications after reshaping surgery.
Electrospun nanofibers have distinguishing characteristics. These include nanoscale diameter, high surface-area-to-volume ratio, biodesign, and tuneable chemical and electrical properties [5, 6]. Numerous studies support the potential of designed nanofibers to control cell morphology, cell migration, and other convoluted biological processes (e.g., differentiation of extracellular matrix (ECM)) via topography and structure analyses [7, 8]. These features have placed electrospun fibbers at the center of attention in biomedical settings such as tendon repair.
In this context, the present study proposes a new surgical procedure for stabilizing the repaired tendon. For this purpose, and according to previous studies, the nanofiber scaffold is designed and fabricated as a synthetic pulley. This method is alleged to facilitate healing when treating this medical condition.
First, the strength, dimensions, and configuration of pulleys A2 and A4, and the features of a natural pulley, are theoretically obtained by studying medical textbooks and biomechanical tests on the corpse. Then, using the obtained data, the synthetic pulley is structurally designed.
The present study aims to fabricate a synthetic pulley as a porous scaffold that allows cells to penetrate the scaffold and become a natural tissue. The electro-spinning-triggered implantation, multiplication, and differentiation of cells allow ECM formation inside the scaffold. Then, the synthetic pulley gradually becomes a natural tissue [9]. Thus, using PU elastic polymer with proper degradability and good tensile properties and strength is favourable for constructing synthetic pulley scaffolds [10]. This is because, despite considerable research, fabricating synthetic pulleys with maximum opening and lowest clinical problems is challenging. This way, the present study employs the electro spinning method for fabricating PU-based synthetic pulleys with their nano-sized, fibrous, and porous structure. The structural analysis results, mechanical properties of scaffolds, and comparison of the results with the mechanical properties of natural pulleys are separately discussed in the following sections.

Materials

In this study, polyurethane (PU) and PU solvents [including N, N-Dimethylformamide (DMF), and tetrahydrofuran (THF)] were utilized. In addition, ethanol 99.6% was used for the separation of scaffolds from the collector. The physical properties of the above materials are given in Table 1. The purchased materials were used with no purification.

Methods

PU nanofiber solution and electro spinning

For PU polymer, according to [11-13] and tests carried out in this study, the optimum conditions were considered as initial conditions for making PU solution and its electro spinning. To do so (as shown in Figure 1), the adequate volume of this polymer was solved in a mixture of DMF and THF solvents with a 1:3 ratio and stirred overnight on a low-speed magnetic stirrer. The polymer was ultimately electrospun under conditions specified in Table 2.

Table 1: The specifications of solvents used in the present study						
Solvent	Chemical formula	Molecular mass (g/mol)	Density in 20 ºC (g/ml)	Dielectric constant (ε)	Boiling point (ºC)	Company
Ethanol 99.6%	C2H6O	46.07	0.789	24.5	78.24	Merck (Germany)
DMF	HCON(CH3)2	73.09	0.994	38.3	153	Merck (Germany)
THF	-CH2(CH2)3O-	72.11	0.889	7.6	66	Merck (Germany)

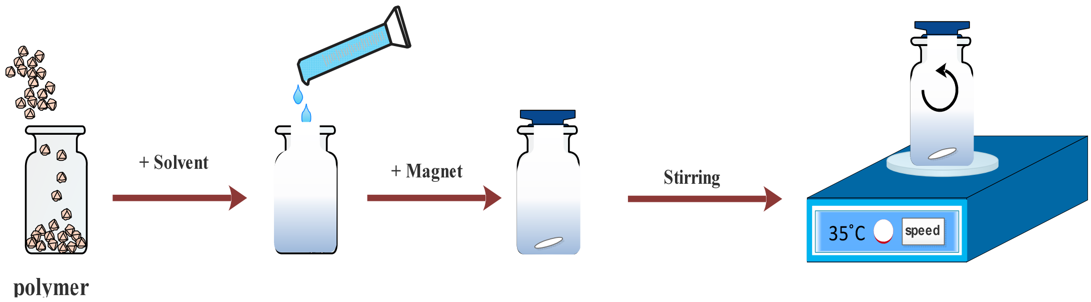

Figure 1: Steps to make a polymer solution

Table 2: The initial conditions for PU electro spinning						
Polymer	Solvent	Concentration	Voltage (kV)	Distance (cm)	Discharge (mh.hr)	Needle (G)
PU	DMF/THF (1:3)	15 w/w%	25	25	3	18

Field emission scanning electron microscopy (FESEM)

The structure of the fabricated nanofiber was analyzed by scanning electron microscopy (SEM) imaging. For this purpose, the inner surface of gold-plated specimens was imaged by SEM (Models VEGA II TESCAN and MIRA II TESCAN) with an accelerating voltage of 15 kV. The images were then analyzed in IMAGE J software. The results of fibber diameter distribution for each specimen are given in the following sections.

Porosity

The porosity of each scaffold is evaluated as the ratio of the volume of all pores and the total volume. This parameter is paramount for substituting synthetic pulleys due to cellular implantation. In the present study, based on the review of previous studies, the gravimetry method was used to measure the porosity of specimens. The equations utilized in this method are discussed in the following.

The apparent density of scaffolds is measured from Equation (1):

$$\rho_A = \frac{m_s}{A_s T_s} \quad (1)$$

Where (ρ_A), (m_s), (A_s), and (T_s) are, respectively, the apparent density (gr/ml), the mass of scaffold (gr), the scaffold's surface area (cm^2), and the thickness of scaffold (µm). The porosity (ε) of single scaffolds is obtained from equation (2), provided that the bulk density of scaffolds is specified [(14)]:

$$\varepsilon = \left(1 - \frac{\rho_A}{\rho_{bulk}}\right) \times 100 \quad (2)$$

Where (ρ_{bulk}) is the bulk density, its value for PU polymer is 1.17 gr/cm^3.

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Fourier transforms infrared spectroscopy (FTIR)

FTIR works based on the absorption of infrared radiation and analyzing vibrational mutations of molecules and polyatomic ions to determine the functional groups of polymers in polymer blends [(15)]. This method identifies organic compounds and functional groups in a given specimen. In the present study, FTIR analysis was carried out in a Perkin Elmer C-92264 spectrophotometer. For this, a given volume of fabricated scaffolds was blended and compacted with potassium bromide (KBr). Then, the blend was put into the spectrophotometer with a holder from 400 cm-1 to 4000 cm-1.

Mechanical tests

The primary mechanical properties concerned in this study are stress, strain, and Young's modulus. These properties were investigated based on specific requirements set by the American national standard ISO 7198 and are discussed in the following.

Ultimate tensile stress (UTS)

The "axial tension" was measured for three specimens of each scaffold (n = 3) using Instron 5566 Testing Machines for Tensile (USA). Each scaffold was cut rectangularly (2 cm in length and 0.5 cm in width). The specimens then underwent a 10 N tensile force at a rate of 2 mm/min ram speed until breakage, and their tensile properties were ultimately measured.

Strain at UTS point

The other critical parameter in the tensile test is strain. This parameter defines a ratio of the change in the specimen's length to the original length. Strain at the UTS point is a change in the scaffold length when the scaffold is under the maximum force applied.

Young's modulus

The stress-strain curve is, in turn, the most important output of the tensile test. The curve's linear or elastic zone slope is known as Young's modulus [(16)]. Young's modulus indicates strength in individual structures.

Results

SEM images and determination of the mean fibber diameter and porosity

FESEM images, mean diameter of fibbers, and porosity of individual PU fibber structures are shown respectively in Figure 2 and Table 3.

As shown by FESEM images, the fibbers are bead-less and nano-sized.

Accordingly, the electro spinning process has allowed the fabrication of nanofibrous scaffolds with 470 nm fibber diameter and proper porosity.

Mechanical properties

Calculation of tensile stress, strain, and Young's modulus in individual PU structures

According to the results in Table 4, PU nanofiber scaffolds possess optimum elasticity (321 ± 71%) and have a strength value of 1.20 ± 0.39. Table 4 further gives the results obtained for natural pulleys. A comparison of the mechanical properties of natural pulleys with PU nanofiber structures shows that the latter could be used as synthetic pulleys. As per the results, the strength (Young's modulus) required to simulate the synthetic structure for pulley substitution equals 1.06 ± 0.17 (0.69 ± 0.07 MPa). The corresponding value for the structure of PU nanofiber scaffolds is 1.20 ± 0.39. As confirmed by the results, the fabricated scaffold can provide the required strength. Furthermore, PU scaffolds with an elasticity of 321 ± 71% can provide the elasticity required when utilized as synthetic pulleys. The maximum force-bearing and stress values in PU nanofiber structures are close to that of natural pulleys (Table 4).

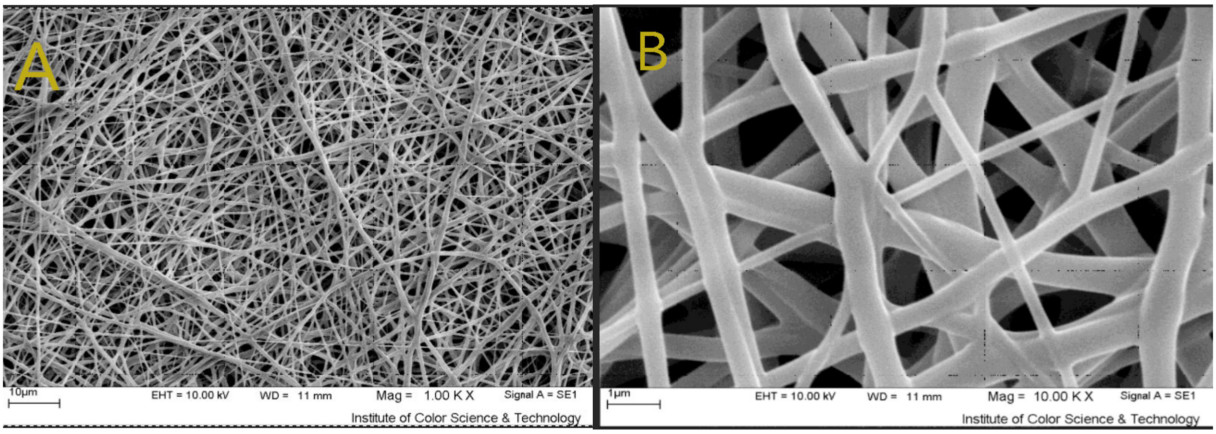

Figure 2: SEM images of PU nanofiber structures at magnifications of A) 1.00 KX and B) 10.0 KX

Table 3: Mean diameter of fibbers and porosity of PU individual structures

Specimen	Mean fibber diameter (nm)	Porosity (%)
PU	470 ± 95	63.0 ± 0.46

Table 4: Mechanical properties (maximum force-bearing, stress, strain, and Young's modulus) in PU individual nanofiber structures

Specimen	Max force-bearing (N)	Ultimate stress (MPa)	Ultimate strain (%)	Young's modulus (MPa)
PU	7.26 ± 0.96	3.19 ± 0.54	321 ± 71	1.20 ± 0.39
A2	3.005 ± 0.21	0.966 ± 0.09	109 ± 11	1.06 ± 0.07
A4	5.07 ± 04	0.759 ± 0.05	31 ± 8	0.69 ± 0.07

Discussion

Flexor tendon injuries are common and yet highly challenging medical conditions. The treatment choices include suturing, auto grafting, and allografting. Currently, the commonly used procedure for repairing a ruptured tendon is suturing. However, this procedure is associated with problems due to the complexity of the surgery, a long-drawn-out process, the risk of sticking the sutured tendon to the surrounding tissue, and fibrosis [17]. In addition, the prolonged healing process, substantial medical costs, pain, and discomfort are expected due to the weak mechanical strength at the suture site. In this regard, early motion and exercise are advised to avoid tissue sticking in the flexor tendons of the hand. Through this procedure, both ends of the ruptured tendon are stuck by bridging the gap between the tendon ends by suturing. However, the stitches do not provide the strength required for active tendon movements. Thus, the surgeons should hold the operated finger (hand) fixed for at least two months, leading to tissue sticking due to fibrosis [18]. Significantly, not all tendons are fully reconstructed by this procedure, and they lack optimum functioning and require strength after repair. Therefore, alternative treatments, such as using synthetic pulleys, are critical. For a successful clinical application, designing a structure with high strength after repair, resisting mechanical forces during rehabilitation and avoiding sticking the tendon to the surrounding tissue is the most appealing. To avoid these complications, synthetic pulleys are proposed as tendon protection implants. In light of these, the synthetic pulleys with PU nanofiber structures were fabricated in this study, and their structural and mechanical properties were evaluated. As a structure constituting body tissues and a frame to hold cells together, ECM is a 3-D structure made of protein and polysaccharide fibbers with a diameter between 50 to 500 nm [11]. Nanoengineering technology refers to the design, synthesis, characterization, and application of materials whose functional structure is nano-sized at least in one dimension. This technology works based on altering the properties of materials to a great extent by reducing their dimensions to the nanoscales, such that the new material has properties that differ vastly from the original material. Nanofibers are highly important (among other nanomaterials) due to their potential applications [19]. Electrospinning is a multifaceted method to produce ultrafine (in micro/nanometer) fibbers. Electrospinning is more trivial than other methods due to more structure development, which is bio-inspired by the natural ECM microenvironment [20]. The electrospun fibbers are thus claimed to be potential scaffolds in engineering applications due to their decisive role in controlling interactions between the engineered tissue and the body and their power to simulate the ECM of body tissues [21]. In the present study, the structural analysis of the PU scaffold made by electro spinning confirms the similarity of the synthetic structure to the ECM of the body with nanometre dimensions and porosity comparable to that of the body's natural tissues. In addition, PU polymer is highly elastic and has two soft and rigid components. The rigid component provides relative strength in this polymer, while the soft one provides the elasticity of the nanofiber scaffold. A comparison of the mechanical properties of the synthetic PU scaffold with that of natural pulleys shows that this structure could be efficiently used as a synthetic pulley. Concerning the obtained mechanical properties, the value of Young's modulus in PU scaffolds is remarkably close to the corresponding value in natural finger pulleys. Regarding the optimum mechanical properties of PU polymers approved by the FDA and their successful applications in synthetic vessels [11, 22-24], the present study fabricated synthetic pulley scaffolds with porous nanofiber structures via electro spinning. Then, the mechanical properties of the scaffolds were evaluated. The results revealed that the designed structure is a good candidate (as a synthetic pulley) for tissue engineering applications.

Conclusion

In the present study, PU nanofiber scaffolds were designed and fabricated as synthetic pulleys. The fabricated scaffolds had a nanofiber structure and were randomly dispersed and bead-less. The size of scaffold fibbers was comparable to that of ECM in natural body tissues. The functional groups obtained from FTIR confirmed the PU polymer and happening of no unwanted reactions in the structure. The mechanical properties (stress, strain, and Young's modulus) have been investigated in corpse fingers. According to the analyses, the mechanical properties of PU nanofiber structures are close to those found in natural pulleys, allowing these structures to be used as synthetic pulleys.

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