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Gelatin yarns inspired by tendons — Structural and mechanical perspectives

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ABSTRACT

Tendons are among the most robust structures in nature. Using the structural properties of natural tendon as a foundation for the development of micro-yarns may lead to innovative composite materials. Gelatin monofilaments were prepared by casting and spinning and small yarns—with up to ten filaments—were assembled into either parallel or 15° twisted yarns. The latter were intended as an attempt to generate mechanical effects similar to those arising from the crimp pattern in tendon. The mechanical properties of parallel and 15° twisted gelatin yarns were compared. The effect of an increasing number of filaments per yarn was also examined. The mechanical properties were mostly affected by the increasing number of filaments, and no benefit arose from twisting small yarns by 15°. However, since gelatin filaments are elasto-plastic rather than fully elastic, much increased toughness (by up to a factor of five for a ten filament yarn) can be achieved with yarns made of elasto-plastic filaments, as demonstrated by experiments and numerical simulations. The resulting effect shows some resemblance to the effect of crimp in tendons. Finally, we developed a dependable procedure to measure the toughness of single filaments based on the test of a yarn rather than on a large number of individual filament tests.

1. Introduction

In the course of the last decades efforts have been made to develop grafts of soft connective tissues (e.g. blood vessels, tendons, ligaments) by means of a biologically-inspired strategy [1–3]. Thorough understanding of these soft tissues in conjunction with the progress achieved in biomedical synthetic components, indicates that synthetic collagen fibers offer significant advantages over traditional polymers for soft tissue repair and replacement [4].

A tendon is a soft connective tissue that generally experiences forces that are purely longitudinal and tensile as it transmits the contraction of muscle to bone [5]. It is one of the toughest structures found in nature. Emulating the tendon's unique characteristics may bring about the use of wires or ropes that may function as active components to generate, transmit, and convert power and motion. Such a bio-inspired approach may stimulate innovative thinking in the structural design of future engineering composite materials. The main goal of the present paper, which rests on the observed mechanical toughness of natural tendon, is to develop a bio-inspired and bio-compatible implantable yarn material based on porcine skin gelatin.

The tendon presents a unique hierarchical structure in which all levels of organization from the molecular through the macroscopic are oriented to optimize the reversible and irreversible tensile properties along the length of the tendon without fracture. Its most fundamental levels consist of tropocollagen helix molecules. The multi-level organization imparts toughness to the tendon [6–8]. The hierarchical structure of tendon includes collagen fibrils that have a wavy appearance, characterized as a planar zigzag. This crimp waveform is gradually straightened when the tendon is stretched along its length, and its magnitude determines the reversible elastic properties of the tendon [6]. The crimp could also have a toughening effect as the tendon strain progressively increases with uncrimping.

The primary constituents of tendon are water and type I collagen [5]. Collagen's main role is to provide structural integrity to the tissue. Collagen, as a fibrous, structural protein is composed of a right-handed bundle of three parallel, left handed helixes of polyproline type II. The resulting triple helical structure is called tropocollagen [6,9–11].

Generally, the mechanical properties of biological materials (such as collagen) and structures are of great significance to virtually all physiological properties at each and every scale [12]. Among biomaterials, collagen-derived gelatin is particularly interesting. In a dehydrated state, gelatin is a partially crystalline polymer with a relatively low melting point in the range of 40 °C–150 °C, depending on the amount of plasticizer used [13,14]. Gelatin is a very important polymer, primarily used as a gelling agent forming transparent, elastic, thermo-reversible

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gels at room temperature. Currently, it is mainly used by industries in the food and pharmaceutical sectors (with analog photography industries being important historical users), but it has several other technical applications [9]. Gelatin is a high molecular weight and water-soluble protein produced through thermal denaturation of collagen. Although it has lower strength and stiffness than collagen, it is easier to extract and prepare than collagen and thus more practical and economical to use [15–17]. Through the thermal denaturation of collagen (collagen–gelatin transition process), the highly organized, water insoluble collagen fiber transforms from an infinite, asymmetric network of linked tropocollagen units to a system of independent, water-soluble molecules with far less internal order [18]. Depending on the treatment of collagen, either gelatin type A or gelatin type B can be obtained, where the former is extracted from collagen by acid treatment, while the latter is extracted by alkaline treatment [19].

Two main sources for the preparation of gelatin are bovine and porcine collagens, which have been implanted clinically for decades and whose hydrolysis products, i.e. bovine and porcine skin gelatins, are widely utilized in food industries. However, porcine skin gelatin (of type A) is stiffer than bovine skin gelatin due to its high degree of cross-linking as well as the significant amounts of glycine and proline contained in it [15,20]. In addition, the hydrogen bonds in porcine skin gelatin between water molecules and free hydroxyl groups of amino acids positively influence gelatin strength [21]. For these reasons, porcine skin gelatin was selected for this research.

The mechanical and thermal properties of gelatin are related to its denaturation level, i.e. the triple helix content of the protein. These properties are substantially influenced by parameters such as molecular weight, polydispersity, thermal history, water content, and the time and mode of drying[9,22–24].

Gelatin based materials are hygroscopic materials that are very sensitive to environmental conditions, such as temperature and relative humidity [25]. The gelatin structure forms a three-dimensional network containing zones of inter-molecular microcrystalline junctions. When this system is dehydrated, it may result in brittle structures. This can be prevented by the addition of plasticizers to reduce interchain interactions and improve film flexibility [26]. A widely used plasticizer is Glycerol, which is non-volatile and has constant mass during aging of the films [14]. Gelatin based materials with plasticizer have sufficient stability, strength and flexibility to be useful for making films, monofilaments and fibers that can serve as reinforcements for composites [13], or used for yarns.

Yarns are typically interlocked fibrous bundles constituting a basic building block for complex fibrous architectures [27]. Usually, the fibers within the yarn are twisted, mainly to achieve a coherent structure that cannot easily be split by lateral actions. This configuration provides continuous yarn integrity and forces the array of multiple fibers to behave as a single unit. However, twisting results in lower yarn strength due to fiber obliquity; moreover, fiber damage may appear when a high degree of twist is applied, with potential yarn strength reduction [28–30]. Although the effects of yarn twist remain debatable, its application does result in a more intimate interaction between fibers than in a loose yarn made of parallel fibers. This, of course (as well as the filament length which is not considered here) influences the strength and modulus of a yarn, as well as the strength variability [31–33]. Various theoretical models of Young's modulus and strength of twisted yarns have recently been reviewed by Sui et al. [30].

Twisted yarns composed of (twisted) fibers have a unique strength-generating mechanism, in which the force that is breaking the structure is strengthening it at the same time [28]. In other words, on the one hand there are variables such as inter-fiber friction and lateral contractions due to fiber twisting that reduce the tensile strength of the yarn, while on the other hand there are rope unwinding mechanisms that, similar to waviness release in natural tendon, amplify ductility [4,30,32,33]. Such a mechanism is bound to give rise to complications, with the yarn strength predicted to be smaller than the constituent fiber strength. This insight confirms that yarn strength is not strictly an intrinsic property of its constituent materials. Rather, it is also dependent on the yarn structure as well as on loading conditions [28].

Here we investigate the tensile mechanical behavior of micro-scale yarn specimens made of a small number of gelatin micro-filaments. The main parameter is the number of filaments (in resemblance to the hierarchical structure of a tendon composed of different layers), in both parallel and twisted configurations.

2. Materials and methods

2.1. Preparation and drying of gelatin film

For the purpose of producing gelatin fibers, gelatin films were prepared with an initial composition of 0.005 wt.% sodium azide (Riedel-deHaën, India), 67.5 wt.% three distilled water (TDW), 5.4 wt.% glycerol (Gadot, IL) and 27 wt.% gelatin (pigskin gelatin, 300 Bloom, Sigma Aldrich, IL).

Sodium azide (used as a preservative) was dissolved in TDW. Subsequently, glycerol (used as a lubricant) was added, followed by gelatin which was added and mixed gradually. The resulting solution was immersed in an oil bath at 85 °C for 3 h. Afterwards, it was poured into a Teflon mold and transferred to an incubator (at a constant temperature of 25 °C) which contained silica for stabilization overnight. After stabilizing, the resulting film was cut into strips and dried in an incubator for 4 additional days, until its water content got down to 20% [13]. The water functioned as the main plasticizer. Hence, it was very important to control the drying process to reach a 20% water content prior to extrusion. For this purpose, Thermo Gravimetric Analysis (TGA) measurements (Mettler Toledo, TGA/DSC 1 STAR^e system) were performed repeatedly to measure the amount of water in the specimens. The thermal method consisted of heating from 20 °C until 200 °C at a heating rate of 10 °C/min, in a nitrogen atmosphere [34].

Eventually, the chosen composition of the film right before extrusion was 0.005 wt.% of sodium azide, 20 wt.% of TDW, 10 wt.% of glycerol, and 70 wt.% of gelatin.

2.2. Filament preparation and storage

To prepare a filament, the film strips were cut into square pellets that were then fed via a hopper into a twin-screw micro-compounder/extruder (DSM, Xplore, 15 cc, Geleen, Netherlands) used for hot-melt extrusion. The micro-compounder barrel was subjected to a nitrogen atmosphere and was gradually heated to 105 °C, which was the extrusion (die) temperature. The resulting filaments were stored in a closed container to which Magnesium–Hexa-Hydrate ($MgCl_2{}^*6H_2O$) was added (to preserve humidity of around 35% by balancing the salt vapor pressure and that of the air). This was done to guarantee a constant level of water in the filaments.

2.3. Sample preparation

Filaments prepared by a hot-melt extrusion method were cut into 12 cm long specimens. These filaments were photographed with an optical microscope (Wild Heerbrugg, model 4680) connected to a camera (Moticom 1000, 1.3 M pixel, USB 2.0) using a computer program that enabled high-resolution images. Their diameters were typically about 400 μm, as measured with ImageJ software. To prepare yarn specimens with a parallel configuration, the filaments were simply attached to each other and glued at the edges. Twisted yarn specimens were prepared with a manual device in which parallel filaments were gripped between a fixed and a swivel clamp. The latter was turned around by a crank shaft and the degree of twist was measured with ImageJ. The twist angle is defined as the angle between a filament direction and the central axis.