

Textile structures from hyaluronan based core-shell fibers

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Abstract. Core-shell fibers based on the combination of soluble and insoluble types of hyaluronan were successfully created using wet-spinning method. High swelling of the fibers in synergy with tight textile structures were employed to ensure release of the dissolved fiber core through local cracks in the fiber shell. Thanks to the biocompatibility and resorbability of hyaluronan, the braided or knitted textile structures made from these fibers have a potential to be employed as a drug carrier in medical applications.

1. Introduction

Hyaluronic acid (HA) or briefly hyaluronan is a natural polysaccharide composed of D-glucuronic acid and N-acetylglucosamine. It is contained in the human body, e.g. in extracellular matrix, synovial fluid, eyes and skin. Thanks to its biocompatibility and biodegradability, HA is commonly used in cosmetic and pharmacy [1,2]. Hyaluronan can have various forms suitable for different medical applications, e.g. hydrogels for tissue engineering and viscous solutions or freeze-dried layers for wound healing. Also fibers and textiles based on hyaluronan derivatives has been already developed and utilized in surgery to improve tissue regeneration [3,4]. A fabrication of the textile scaffold based on hydrophobized HA was reported in another paper [5]. Because hyaluronan is not a meltable polymer the fibers thereof can be formed just using a solution spinning process.

Hyaluronan in its natural form is soluble in water but using a chemical modification an insoluble variant can be obtained. This can be advantageous in various medical applications in which a prolonged stability of the fibers in a tissue is required. Anyway, such modified fibers still swell a lot when dipped in a water-based medium, including various body fluids, e.g. blood, wound exudate or saliva. A wet-spinning process that allows the formation of hyaluronan-based monofilaments has been invented in Contipro [6,7]. This process is suitable both for the natural HA and for its hydrophobized derivatives.

The aim of our consequent work was to develop a fibrous system utilizable as a carrier of active substances in medical applications. The basic idea was to create a bicomponent fiber comprising of two different derivatives of hyaluronan arranged separately as a core and shell of the fiber. It was expected that native hyaluronan which is soluble in water would carry an active substance whereas an insoluble derivative of hyaluronan would ensure mechanical compactness of the fiber in wet conditions. An extensive effort was made to obtain fibers with sufficient tensile properties and flexibility which would allow them to be processed by textile techniques like knitting or braiding to create a fabric.

Within textile structures (woven, knitted, braided) yarns are mutually interlaced and touch each other in cross points. The geometry of the yarn axis relates to the fabric pattern, the yarn diameter and the



tightness of the textile structure. If fibers within the yarns shrink and/or swell when dipped in water the fabric gets closer and tighter which results in the fabric shrinkage. This phenomenon has been studied in the relation with washing of cotton fabrics [8]. Anyway, if the fiber swelling and/or shrinkage is much higher than in case of cotton then these dimensional changes can cause enormous tensile stress in the fibers and result in their break.

As mentioned above a critical property of hyaluronan-based fibers is their huge swelling in a water-based medium. Therefore, this study is focused not only on the properties of the HA-based core-shell fibers in the dry state but also on the behavior of the textile structures when they interact with water.

2. Materials and Methods

2.1. Hyaluronan and its derivatives

A range of hyaluronan based polymers of Contipro production was used for manufacturing of the core-shell fibers. The water-soluble variant of hyaluronan was sodium hyaluronate (SH) of molecular weight (Mw) of 1,6 MDa. The insoluble variants included HA derivatives (HA-der) acylated by fatty acids (palmitic, oleic, stearic) with different degree of substitution (DS).

2.2. Spinning process

The core-shell fibers were created by extrusion of two different polymer solutions through a two-way coaxial spinneret to a coagulation bath. In some cases, the spinning solution contained a functional agent, e.g. iron oxide nanoparticles (NP) or a drug (octenidine dihydrochloride). Various process parameters incl. concentrations of the spinning solutions, extrusion rate and up-winding speed were used to obtain fibers of different fineness and ratio between the core and shell components. Finally, the fibers were scoured in ethanol to remove residues of the coagulation bath and dried at room temperature.

2.3. Fiber fineness and geometry

The fiber fineness was determined by weighting of fiber segments of 1 m length. The geometry of fibers was studied by scanning electron microscopy (SEM) using the microscopes Tescan VEGA II LSU and ZEISS Ultra Plus and by optical microscopy (Nicon Eclipse Ci-L). Ratio between the core and shell fiber component was calculated from the concentrations of the spinning solutions and their extrusion rates. Swelling properties were determined by dipping of fibers in demineralized water and measuring their diameter.

2.4. Tensile test

The tensile strength and the elongation at break were measured on the dynamometer Instron 3343. The measurement was executed at 23 ± 2 °C and relative humidity of 50 ± 5 %. The test length was 100 mm and the elongation rate was $30 \text{ mm} \cdot \text{min}^{-1}$.

2.5. Textile technologies

2.5.1. Braiding. The horizontal braiding machine Steeger HS 80/48 VEA was used to produce a tube from 16 monofilaments interlaced in the twill pattern. Two variants of the tube were made:

- a) A tube with a hollow inside
- b) A tube with a steel wire of 0.5 mm diameter additionally inserted into the hollow

The braiding density of both tubes was 13 picks/cm, braiding angle 30° and the outer diameter 1.25 mm.

2.5.2. Knitting. The raschel machine Comez DNB-EL of gauge 12 was employed to prepare a narrow strip of single-faced tricot patterned fabric with the closed loops. The loop density was:

- a) 4 wales/cm, 5 courses/cm
- b) 5 wales/cm, 7 courses/cm

3. Results and discussion

3.1. Fiber morphology

The HA based core-shell fibers have a form of monofilaments with an irregular shape of cross section which is caused by the coagulation process and the consequent drying (see the figure 1). The fineness of such fibers is in the range of 10 to 40 tex which corresponds with the diameters of 100 to 300 μm (despite the non-circular cross-section of fibers the term diameter is used in this paper and it means thickness of an individual fiber). The ratio between the core and shell components is between 1:1 to 1:5. Determination of the boundary between the core and shell on the cross section can be sometimes difficult when using SEM. Alternatively it can be detected using optical microscopy thanks to different optical properties of SH and HA-der or if a colored agent (e.g. NP) is incorporated in the fiber core.

Examples of the HA based core shell fibers and their properties are listed in the table 1.

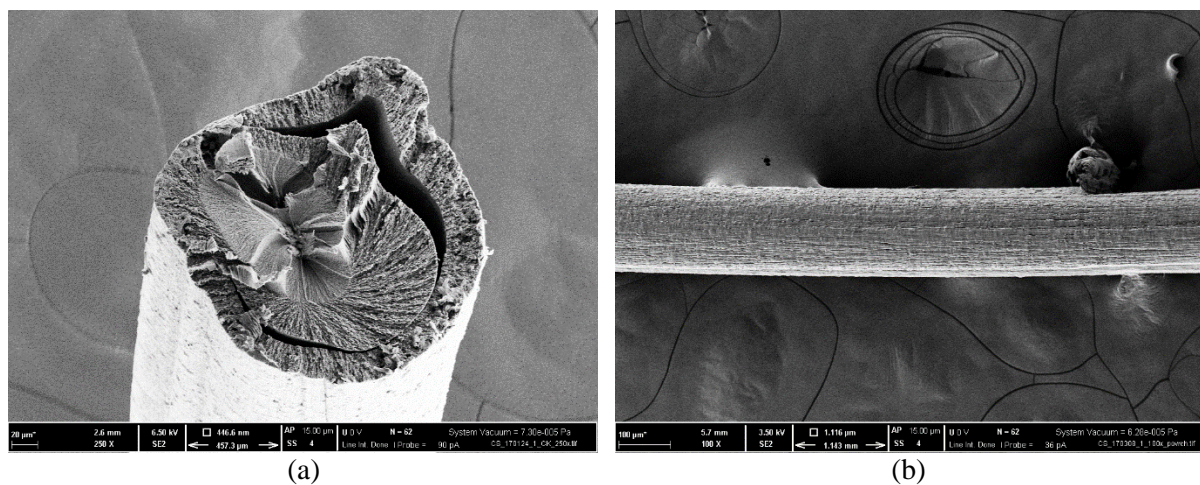


Figure 1. Morphology of the core-shell fiber based on hyaluronan: (a) cross section of the fiber (scale bar 20 μm) (b) longitudinal view (scale bar 100 μm).

3.2. Mechanical properties and processability

The tensile strength of the fibers is between 0,05 and 0,1 N/tex which is lower than most of the conventional fibers. The mechanical properties of the HA based fibers strongly depend on the air humidity: if the humidity is low the fibers get brittle and tend to break when processed. The fibers have quite high bending rigidity thanks to their high diameter which complicates their processability too. Thus, gentle mechanical conditions and appropriate air humidity (50-60%) must be ensured during mechanical processes like knitting or braiding.

Table 1. Examples of the hyaluronan based core-shell fibers.

Core	Shell	Core-shell ratio	Fineness [tex]	Strength [N]	Breaking elongation [%]
SH	der-HA	1:3.5	19	1.46	12.3
SH	der-HA + NP	1:5.0	32	2.62	8.1
SH	der-HA + drug	1:2.5	20	1.97	15.4
der-HA	der-HA	1:2.0	20	1.11	9.5

3.3. Fiber swelling

When the core shell fiber is dipped in water both the core and shell absorb a lot of the liquid. The SH core begins to dissolve whereas the insoluble HA-der shell just swells. The difference between the dry fiber and the swollen fiber is shown in the figure 2. The swelling rate is quite high: the fiber diameter can increase more than thrice within several minutes as documented in the figure 3. This swelling results in the pressure on the core; if the fiber is dipped completely including its cut ends the dissolved SH is pushed out of the core towards the fiber ends. The core works like a hose and a pump in the same time which results in spilling the core out of the shell part.

The fiber swelling depends on the liquid media, on the selected variant of the HA derivative and on the degree of substitution. As the degree of substitution increases the fiber swelling decreases.

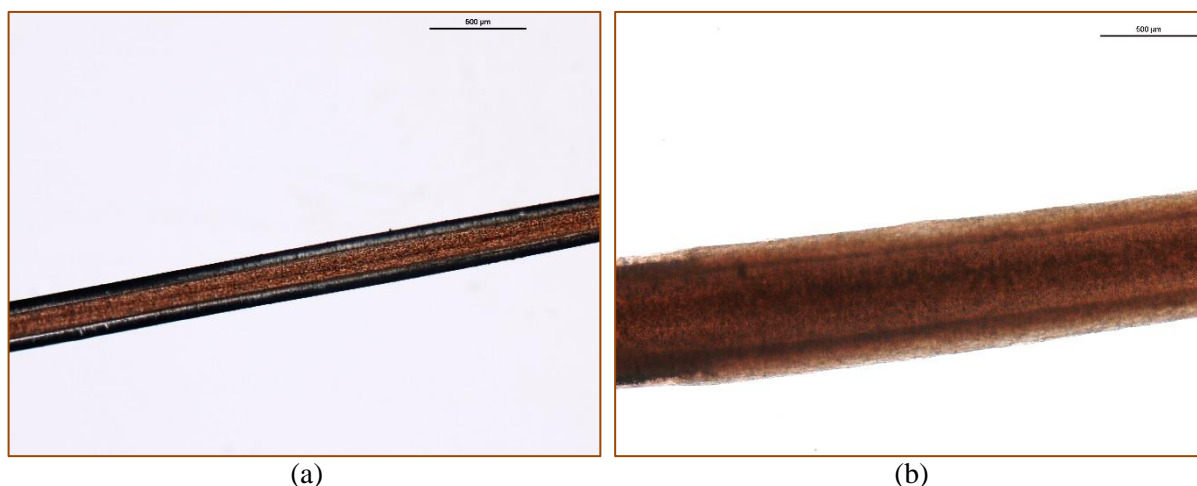


Figure 2. HA based core-shell fiber containing nanoparticles in the soluble core: (a) in the dry state and (b) in the swollen state after dipping in water (scale bars 500 μm).

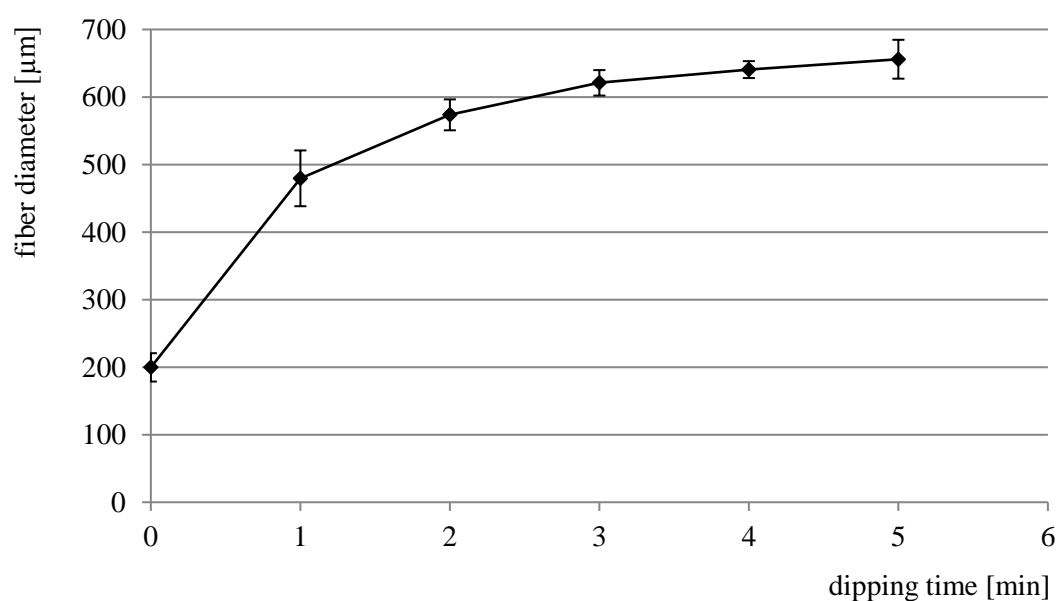


Figure 3. Swelling of the HA based core-shell fiber after dipping in demineralized water: Changes of the fiber diameter in dependence on the time.

3.4. Shell ruptures and core release

The huge increase of the fiber diameter causes significant changes of the textile structure. As the fibers swells a textile structure gets tighter and a free space between fibers decreases. Moreover, the swollen core-shell fibers press to each other in cross points. We could see that in some cases the mutual pressure in the cross points resulted in the shell disruption. Anyway, the fibers did not break fully but just local cracks were created randomly at different places of the textile so that the textile structure remained compact. The local shell ruptures of the fibers within a braided and knitted textile can be seen in the figure 4. It seems that the cracks often arise in places where the fiber is bended over a neighbouring one.

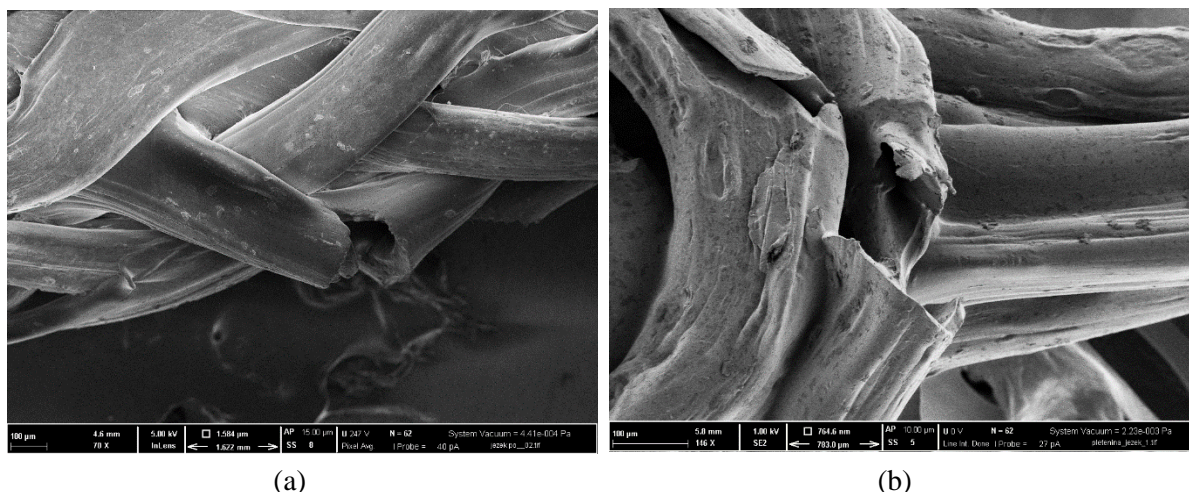


Figure 4. Ruptures of the shell part of the fibers arisen from swelling: (a) a rupture in the cross point of the braided tube (b) a rupture in the cross point of the knitted fabric (scale bars 100 μm).

The cracks in the fiber shell allow the dissolved fiber core to spill out of the fiber. This phenomenon is shown in the figure 5: Swelling of the fibers within a braided tube resulted in local shell ruptures. The places where the core spills out can be seen thanks to the brownish color of the nanoparticles contained in the fiber core. The ruptures only arose on the variant with the wire inserted inside the tube. In the other case (with the hollow inside) the pressure between the fibers were not so high to disrupt the fiber shell probably because the inner segments of the swollen fibers could deflect to the free space inside the tube. Disruptions of the fiber shell followed by spilling of the core were observed also at knitted fabrics.



Figure 5. Braided tube from HA based core-shell fibers with nanoparticles in their core: (a) dry state (b) swollen state – spilling of the dissolved core is visible as brownish smudges (scale bars 1000 μm).

3.5. Possibilities of the controlled drug release

Based on our preliminary experiments we know that various drugs can be incorporated into the fiber core. We suppose that the above described “rupture effect” and the consequent spilling of the dissolved core can be utilized for the controlled drug release: in the dry conditions the fibers would hold a drug inside but as soon as the fabric gets in contact with a body fluid (e.g. blood or wound exudate) the drug release would be ensured via the spilling the liquid core through the cracks caused by swelling.

The inception of the rupture effect and the progress of the core spilling can be influenced by the fiber composition and by the textile structure. The most important factors will be the hydrophobicity of the fiber shell (DS of the HA derivative), core-shell ratio, way of the fiber interlacement (braided, knitted, woven) and the density of the textile (warp and weft density of woven fabrics, course and wale density of knitted fabrics, braiding density and braiding angle on braids). Optimization of these parameters is one of the tasks for the future research and development of the HA based core-shell fiber systems for medical purposes.

4. Conclusion

Core-shell fibers based on the combination of the soluble and insoluble type of hyaluronan were successfully created using wet-spinning method and further processed by conventional textile technologies. When the fibers are dipped in water they swell significantly and if the textile structure is tight enough then the swollen fibers press to each other in cross points which causes local ruptures. In case the shell is from the insoluble HA and the core from the soluble HA the dissolved core can spill out from the core through these cracks. We expect that such rupture effect can be utilized as a trigger for releasing a drug incorporated in the fiber core after the textile structure gets in contact with a body fluid e.g. at bleeding. Braided or knitted textile structures made from these fibers have a potential to be employed as a drug carrier in medical applications.

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