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Interfacial optimization of fiber-reinforced hydrogel composites for soft fibrous tissue applications

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ABSTRACT

Meniscal tears are the most common orthopedic injuries to the human body, yet the current treatment of choice is a partial meniscectomy, which is known to lead to joint degeneration and osteoarthritis. As a result, there is a significant clinical need to develop materials capable of restoring function to the meniscus following an injury. Fiber-reinforced hydrogel composites are particularly suited for replicating the mechanical function of native fibrous tissues due to their ability to mimic the native anisotropic property distribution present. A critical issue with these materials, however, is the potential for the fiber–matrix interfacial properties to severely limit composite performance. In this work, the interfacial properties of an ultra-high-molecular-weight polyethylene (UHMWPE) fiber-reinforced poly(vinyl alcohol) (PVA) hydrogel are studied. A novel chemical grafting technique, confirmed using X-ray photoelectron spectroscopy, is used to improve UHMWPE–PVA interfacial adhesion. Interfacial shear strength is quantified using fiber pull-out tests. Results indicate significantly improved fiber–hydrogel interfacial adhesion after chemical grafting, where chemically grafted samples have an interfacial shear strength of 256.4 ± 64.3 kPa compared to 11.5 ± 2.9 kPa for untreated samples. Additionally, scanning electron microscopy of fiber surfaces after fiber pull-out reveal cohesive failure within the hydrogel matrix for treated fiber samples, indicating that the UHMWPE–PVA interface has been successfully optimized. Lastly, inter-fiber spacing is observed to have a significant effect on interfacial adhesion. Fibers spaced further apart have significantly higher interfacial shear strengths, which is critical to consider when optimizing composite design. The results in this study are applicable in developing similar chemical grafting techniques and optimizing fiber–matrix interfacial properties for other hydrogel-based composite systems.

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1. Introduction

Physically cross-linked poly(vinyl alcohol) (PVA) hydrogels are extremely biocompatible [1], possess viscoelastic properties similar to articular [2,3] and meniscal cartilage [4], and do not exhibit any wear, even after millions of cycles [5]. As a result, PVA hydrogels have been investigated extensively for articular cartilage applications [2,6]. Poor properties in tension, however, limit the actual use of this material, especially for stronger fibrous tissues similar to the meniscus, ligaments and tendons.

One method to enhance the mechanical properties of polymer networks is through the incorporation of various additives, such as fibers [7,8] and particles [9], the latter including nanoparticles such as clays [10] and nanotubes [11]. Fiber-reinforced composites offer the advantage of easily imparting anisotropic properties to

the material. More importantly, for biomedical applications, cues can be taken from nature to guide composite designs, including fiber layout and orientation, that mimic the native fiber structure of human tissue (e.g. the orientation of collagen fibers in the meniscus [12,13]).

We have previously shown that fibrous reinforcement of PVA hydrogels successfully increased the tensile modulus from 0.23 MPa without any reinforcement to 260 MPa after reinforcement with ultrahigh-molecular-weight polyethylene (UHMWPE) fibers [14], achieving a modulus range similar to that reported in the literature for the native meniscus [15]. UHMWPE fibers were chosen due to their biocompatibility, high strength, high tensile modulus and fatigue resistance [16]. These characteristics are essential in order to withstand the high stresses that occur within joints during movement [17]. The inert and hydrophobic nature of UHMWPE fibers, however, presents a challenge regarding composite processing and ultimate material properties due to poor fiber wettability and interfacial adhesion.

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Oxygen plasma surface modification of polyethylene fibers is a common approach to increase interfacial adhesion [18–21]. Furthermore, the presence of oxygen-containing functional groups on fiber surfaces after plasma treatment allows for chemical grafting of specific functional groups onto the fiber surfaces. We have developed a novel PVA grafting technique to increase interfacial adhesion at the UHMWPE–PVA interface by first activating fiber surfaces with oxygen plasma and then chemically grafting PVA onto the fiber surfaces using an aldehyde linkage. PVA-grafted UHMWPE fibers were then physically cross-linked into the hydrogel network [22].

In this work, the impact of PVA fiber grafting on composite interfacial properties and biocompatibility was evaluated in order to guide future composite design parameters toward soft fibrous tissue applications. Interfacial shear strength was calculated using fiber pull-out tests as a quantitative measure of interfacial adhesion. Interfacial shear strength was determined with and without PVA grafting and as a function of inter-fiber spacing. Scanning electron microscopy (SEM) was used to determine the mode of failure after fiber pull-out. The biocompatibility of PVA-grafted UHMWPE fiber mats was confirmed using a cell-based *in vitro* cytotoxicity test.

2. Materials and methods

2.1. PVA hydrogel synthesis

PVA (>99% hydrolyzed) with a molecular weight of 89,000–98,000 g mol⁻¹ and poly(vinyl pyrrolidone) (PVP) with a molecular weight of 40,000 g mol⁻¹ were obtained from Sigma Aldrich (St Louis, MO). PVP was added in small amounts to the hydrogel formulation to improve network stability through interchain hydrogen bonding [23]. Polymer solutions were prepared by mixing 20 wt.% polymer, composed of 99 wt.% PVA and 1 wt.% PVP, in deionized water. The container was sealed and autoclaved at 121 °C for 2–4 h to ensure complete dissolution of PVA. Polymer solutions were poured into individual cylindrical vials either without fibers (for shear testing) or with fibers (for fiber pull-out testing). Freeze–thawed samples were subjected to 21 h of freezing at –20 °C and 3 h of thawing at room temperature for five cycles.

2.2. PVA shear strength

PVA hydrogels were evaluated in shear, to determine the upper limit for interfacial shear strength. Cylindrical hydrogel samples, prepared as described previously, were ~12 mm in diameter (*n* = 5). To prevent water evaporation prior to testing, hydrogel samples were kept in their sealed vials until immediately before testing. PVA samples were held in place using a two-piece plastic

in-house designed apparatus shown in Fig. 1a. Each plastic piece had a 12 mm diameter indentation. The hydrogels were inserted into the apparatus such that the plastic surfaces for both pieces touched each other. Tensile grips were used to secure the plastic surfaces in place. Testing was performed using an Instron Materials Testing System Series 4442 (Norwood, MA) with a 500 N load cell at a constant cross-head speed, 10 mm min⁻¹, perpendicular to the hydrogel's axial axis. Testing conditions were in air at room temperature and performed until failure. A free-moving metal ring was placed around the two pieces to constrain movement of the plastic to the testing direction. Shear strength, $\tau_{max, shear}$, was calculated as maximum load over cross-sectional hydrogel area according to Eq. (1), where F_{max} is load at failure and r is hydrogel radius.

$$\tau_{max, shear} = \frac{F_{max}}{\pi r^2} \quad (1)$$

2.3. UHMWPE fibers

UHMWPE fibers with a fiber diameter of ~25 μm were obtained from Fiber Materials, Inc. (Biddeford, ME). Fibers were obtained under the trade name Spectra® 1000 in plain weave style 945 with a denier of 215 and reported fiber strength and modulus of 3.25 and 113 GPa, respectively. Single UHMWPE fibers were manually separated from fiber bundles in the weave.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM; Model FEI/Phillips XL30) was used to image UHMWPE fiber surfaces. Samples were carbon coated to prevent charging. Low beam energy, 3 kV, was used to prevent sample destruction during imaging.

2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra were collected using a Physical Electronics PHI VersaProbe 5000 with a scanning monochromatic source from an Al anode. Charging of samples during testing was prevented via a dual beam charge neutralization system. Survey XPS spectra were acquired at 100 W with the following parameters: pass energy of 117.4 eV, range between 0 to 1000 eV, step size of 0.5 eV and dwell time of 20 ms. High resolution spectra were also collected of the elemental C1s peak using the high power mode at 100 W with the following parameters: pass energy of 23.5 eV, range between 278 to 298 eV, step size of 0.2 eV and dwell time of 50 ms. Observed shifts due to charge overcompensation were corrected by shifting the C1s peak to 285.0 eV. Deconvolution of the high resolution C1s peak was performed using CasaXPS processing software. The binding energy

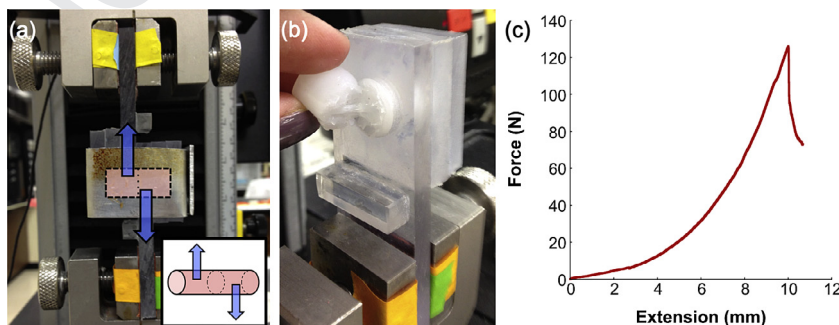


Fig. 1. (a) Shear testing experimental set-up. Hydrogel is shown in pink with blue arrows indicating direction of testing. Inset shows three-dimension view of sample. (b) Failure was confirmed to occur in shear. (c) Typical force vs. extension curve for PVA hydrogels loaded in shear.

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