Poly (vinyl alcohol)-Acrylamide Hydrogels as Load-Bearing Cartilage Substitute

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Introduction: Poly(vinyl alcohol) (PVA) hydrogels have great potential to be widely used as biomaterials for cartilage resurfacing and interpositional devices due to their viscoelastic nature, high water content and biocompatibility. Key material requirements for such devices are high creep resistance to prevent mechanical instability in the joint, accompanied by high water content to maintain a lubricious surface and thus reduce damage to cartilage counterpart during articulation. It has been shown that a highly crystalline, high creep resistant PVA hydrogel can be prepared by high temperature annealing (1). Conversely, the annealing process results in a collapse of the pores, subsequently reducing the lubricity of the hydrogel surface. We hypothesize that a hydrophilic compound such as poly(acrylamide) (PAAm) can prevent the pore collapse by filling the pores during annealing and the hydrophilic nature of the PAAm would increase the ability to retain water subsequently resulting in a hydrogel with high lubricity while still maintaining a high creep resistance.

Materials and Methods: PVA-AAm interpenetrating networks (IPN) hydrogels were prepared by dissolving PVA in deionized (DI) water at 90°C. The solution was mixed with an aqueous solution of AAm monomer at 40°C in the presence of 1:3 ratio of ammonium persulfate to azoisobutyronitrile, for a total initiator concentration of 0.1 w% of AAm monomer. The resulting solution was pre-polymerized at 45°C then poured into a glass mold. The solution was placed in a -17°C freezer for 16 h then thawed for 8 h followed by an 8 h polymerization process (1h to 45°C, 2h at 45°C, 1h to 55°C, 4 h at 55°C). The polymerized IPN was then placed in a -17°C freezer for 16 h with a subsequent 8h thawing. The gel was then soaked in PEG with constant agitation until equilibrium was reached, followed by soaking in DI water in order to remove any unreacted AAm monomer. Water was changed daily and analyzed using the UV-vis spectrophotometer until no trace of AAm monomer was detected. The gels were then dried in a convection oven at 25°C for 14 h, ramped to 80°C in 8 h, then kept at 80°C for 20 h prior to annealing. Annealing was carried out under a 500mmHg argon partial pressure at 160°C for 1 h in a vacuum oven. The annealed gels were rehydrated in DI water until equilibrated. As a comparison, PVA-PEG gels were prepared by mixing 15w% PVA solution at 90°C to 28% PEG (w/PEG)/w(PEG+water) and cooling to room temperature. Two groups were prepared: “as-gelled” (AG) and “de-PEGed” (DP). The latter was immersed in saline solution in order to remove the PEG from the hydrogel and the AG gel was dried similar to the AAm gels, with a subsequent annealing period of 20h at 160°C under argon in a self-pressurized vessel. The equilibrium water content (EWC) was measured using a Thermogravimetric Analyzer (TGA). Creep behavior was determined by applying a 100N load for 10 h followed by a relaxation period under a 10N load for 10 h on cylindrical samples (16mm diameter, 6mm height). The gels were then dried in a convection oven at 80°C in 8 h, then kept at 80°C for 20 h prior to annealing. Annealing was carried out under a 500mmHg argon partial pressure at 160°C for 1 h in a vacuum oven. The annealed gels were rehydrated in DI water until equilibrated. As a comparison, PVA-PEG gels were prepared by mixing 15w% PVA solution at 90°C to 28% PEG (w/PEG)/w(PEG+water) and cooling to room temperature. Two groups were prepared: “as-gelled” (AG) and “de-PEGed” (DP). The latter was immersed in saline solution in order to remove the PEG from the hydrogel and the AG gel was dried similar to the AAm gels, with a subsequent annealing period of 20h at 160°C under argon in a self-pressurized vessel. The equilibrium water content (EWC) was measured using a Thermogravimetric Analyzer (TGA). Creep behavior was determined by applying a 100N load for 10 h followed by a relaxation period under a 10N load for 10 h on cylindrical samples (16mm diameter, 6mm height). The gels were imaged using a confocal laser scanning microscope. Relative coefficient of friction (COF) was determined in DI water at 40°C against an annular fixture mounted on a controlled stress rheometer with an inner radius of 0.72cm and a contact area of 0.36cm² at a constant angular velocity of 0.1 rad/s. The COF between the IPN and the counterface was calculated using the method of Kavehpour and McKinley (2).

Results: Fig 1 shows an increasing pore size with increasing AAm. Fig 2 shows an increase in COF with decreasing AAm. Table 1 shows the tear strength decreased with increasing AAm content whereas both the creep strain and EWC increased with increasing AAm.

Discussion: The equilibrium water content of the IPNs showed an expected increase with increasing AAm concentration, due to the hydrophilic nature of PAAm. The EWC for 15-5, 15-10, and 15-15 PVA-AAm was 50, 72 and 83%, respectively. The EWC of the 15-15 PVA-AAm gel was comparable to that of the 15-28 PVA-PEG AG SRA. Conversely, the pore size of the annealed PVA-AAm gels was significantly smaller than the annealed PVA-PEG (Fig1). Also, the confocal images show an increase in pore size with increasing AAm content. On the other hand, creep resistance of the PVA-AAm gels decreased with increasing AAm (Table 1). Nevertheless, creep resistance of PVA-AAm gels is still higher than that observed on PVA-PEG gels. The relative COF of the PVA-AAm gels was lower than that of the treated PVA-PEG gels (Fig2). The tear strength decreased with increasing AAm content (Table 1). The tear strength observed for the 15-10 PVA-AAm gels was comparable to that of the 15-28 PVA-PEG AG SRA. Conversely, the tear strength of the 15-5 PVA-AAm gels was significantly higher than the rest of the gels. In conclusion, acrylamide addition to PVA hydrogels prevents pore collapse, resulting in IPNs with EWC which still maintain creep resistance and tear strength. The PVA-AAm gels also possess high lubricity. Our results confirm that thermally annealed PVA-AAm IPNs show potential as candidate materials as load-bearing substitutes for human cartilage.


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