

COEFFICIENT OF FRICTION OF POLY(VINYL ALCOHOL) BASED HYDROGELS AGAINST SWINE ARTICULAR CARTILAGE

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Introduction: Non-degradable hydrogel based synthetic materials to repair early cartilage defects in the knee has become a major area of research [1]. One of the most studied polymers for this application is polyvinyl alcohol (PVA) due to its viscoelastic nature, high water content, biocompatibility, tailorable mechanical strength and wide processing window [2]. Thermal annealing is one way of increasing the strength of PVA hydrogel, which also decreases water content and surface lubricity of the hydrogel. This would eventually compromise articulation. In earlier publications we have shown that keeping the pores open during annealing by addition of non-volatile substances (polyethylene glycol, PEG) [1] or adding highly hydrophilic (polyacrylamide, PAAm) [1] and/or ionic moieties such as polyacrylic acid (PAA), [3] the loss of water content and lubricity can be countered. Quantifying the lubricity of these gels against cartilage has been challenging. The purpose of this study was to use a rheometer to measure the torque under a constant normal force and rotational velocity to determine the coefficient of friction of PVA based hydrogels (PVA, PVA-PEG, PVA-PAAm IPNs) against two swine cartilage plugs and compare the values measured against a polished cobalt-chrome (Co-Cr) ring. We also compared the mechanical properties and water content of the hydrogels.

Materials and methods: Preparation of PVA-PAA hydrogel: 25% (19:1 w/w%) PVA-PAA gels were prepared by mixing PVA into an aqueous solution of PAA at 90°C. PVA-PAA solution was poured into pre-heated glass sheet molds and subjected to one freeze-thaw (FT) cycle. The gels were then soaked in PEG400 at 55°C and annealed at 160°C for 1 hour in a vacuum oven. The gels were then immersed in deionized water (DI) at 40°C to reach equilibrium rehydration. A 25% PVA hydrogel was prepared with the same processing steps described above. PVA-PEG hydrogel : 15% (w/w) PVA and 28% PEG solution in DI water at 90°C was molded and cooled to room temperature for gelation for 24h [2]. The gels were then annealed at 160°C and rehydrated in DI water at room temperature (RT). PVA-AAm-IPNs: The PVA-PAA hydrogels were prepared by dissolving PVA in deionized (DI) water at 90°C and mixing with an aqueous solution of AAm monomer in the presence of 1:3 ratio of ammonium persulfate to azobisisobutyronitrile and methylene bis acrylamide (0.01w% of AAm). The resulting solution was polymerized at 55°C, subjected to 1 FT cycle and immersed in PEG400 with constant agitation until equilibrium. The gels were finally annealed at 160°C and rehydrated in DI water at RT. The equilibrium water content (EWC) was measured using a Thermogravimetric Analyzer (TGA). Relative Coefficient of friction (RCOF) was determined against cartilage in DI water at 40°C using a stress control rheometer (AR 2000,

TA Insts). Two cylindrical cartilage plugs of 4.5 mm diameter were mounted onto a fixture. The cartilage plugs were 1.4 cm apart. An annular CoCr ring with an inner radius of 0.72cm and a contact area of 0.36cm² was also used for comparison. Torque, normal force, and velocity data were recorded at a constant angular velocity of 0.1 rad/s, and RCOF between the hydrogel and the counterface was calculated using the method of Kavehpour and McKinley [3]. Creep behavior was determined by applying a 100N load for 10 hours followed by a relaxation period under a 10N load for 10 hours on cylindrical samples (16mm diameter) in DI. The total creep strain (TCS) was reported. Tensile strength was determined by cutting dog bone samples in thick sections according to ASTM D638 and pulling at a rate of 20mm/min on an Instron Insight 2 (MTS) mechanical tester. Ultimate tensile strength (UTS), elongation at break (EAB) and modulus were reported. The articular cartilage samples were harvested from the left knees of 3-month old Yorkshire swine using a 4.5 mm mosaicplasty surgical tool. We measured the RCOF of the PVA hydrogels against one-day frozen cartilage in DI water. TCS and EWC values of the swine cartilage (SC) were also measured.

Results and Discussion: The RCOF values measured against Co-Cr were significantly higher than those measured against cartilage samples (Table 1). Pure PVA hydrogel had the lowest EWC and the highest modulus, UTS, and EAB with a RCOF of 0.4. Although the EWC of the PVA-PEG hydrogel was higher than pure PVA, the RCOF against both Co-Cr and cartilage were the highest among the gels measured (Table 1). Addition of the hydrophilic AAm and AA groups into the PVA network substantially decreased the friction of coefficient while maintaining the EWC and TCS. Their tensile mechanical properties and EWC were comparable to those of pure PVA gel and displayed better creep strain than articular swine cartilage (Table1).

Table1 RCOF, UTS, EAB, modulus TCS and EWC of PVA gels

Sample	RCOF Co-Cr	RCOF Cartilage	UTS (MPa)	EAB (%)	Modulus (MPa)	TCS (%)	EWC (%)
PVA	0.4±0.033	0.09±0.004	13±1	346±60	16±5	6±4	31±2
PVA-PAA	0.07±0.03	0.04±0.001	9±3	293±88	6±0.3	14±5	58±1.2
PVA-PEG	0.4±0.06	0.1±0.001	1±0.1	248±7	2±0.04	60±3	79±0.6
PVA-PAAm	0.07±0.003	0.02±0.001	8±0.3	287±20	5±0.9	23±2	82±2
Swine cartilage	NA	NA	NA	NA	NA	70±2	89±3

Conclusion: RCOF values of PVA hydrogels against cartilage exhibited lower values compared to Co-Cr counterface. PVA-PAA hydrogels were the strongest group of hydrogels with low coefficient of friction against both cartilage and Co-Cr. PVA based hydrogels are promising load-bearing cartilage substitutes for the treatment of early stage cartilage lesions. **Acknowledgements:** Partially funded by a research grant from DePuy. **References:** [1] Bodugoz-Senturk, H et al. *Biomaterials*, 2009, 30 (4): 589-596. [2] Choi, J et al., 54th Annual Meeting of the Orthopaedic Research Society, February 11- 14, 2008, San Francisco, CA, USA. [3] Kavehpour, H.P. et al., *Tribology Letters*, 17(2), pp. 327-335, 2004.