

## Effect of lubricant and the functional group on the coefficient of friction of PVA-Based Hydrogels

Bodugoz-Senturk, H.; Kosztowski, M.; Macias, C.E.; and Muratoglu, O.K.

Harris Orthopaedic Biomechanics and Biomaterials Laboratory, Massachusetts General Hospital, Boston, MA 617-726-3869 Fax: 617-643-2521  
 omuratoglu@partners.org

### Statement of Purpose

Poly(vinyl alcohol) (PVA) is a candidate for synthetic articular cartilage to treat osteochondral defects due to the viscoelastic nature, high water content, and biocompatibility of the hydrogel forms of PVA. However the gels lack strength and toughness. Annealing has been proven to increase the mechanical strength of PVA hydrogels; however it reduces the water content and consequently reduces the lubricity of the hydrogel [1]. Keeping the articulating surface of the hydrogel lubricious is a key requirement to prevent damage against opposing cartilage. Friction in the case of hydrogels is much more complex than solids and it is influenced by a number of factors such as hydrophilicity, charge density, crosslinking density, water content, elasticity, surface properties of opposing substrates, and measurement conditions. It has been shown that one way of improving the lubricity of PVA based hydrogels is the addition of hydrophilic ionic and non-ionic polymers to form IPNs or blends [2]. The positive effect of non-ionic and hydrophilic acrylamide and ionic and hydrophilic 2-acrylamido-2-methyl-1-propanesulfonic acid (AAMPS) on the lubricity of the PVA hydrogels has already been reported by measuring the relative coefficient of friction (RCOF) of these gels [2]. The main focus of this study is to investigate the lubricant-hydrogel interaction and effect of lubricant on RCOF while testing five hydrogels of different chemical structure but with similar water content in three different lubricant solutions: deionized water (DI), saline, and bovine serum based storage media (BSM), the latter of which is a more clinically relevant medium.

### Materials and methods

PVA-AAMPS IPNs were prepared by dissolving 15% (w/w) of PVA, (MW= 115,000 g/mol) in deionized (DI) water at 90°C then mixing at 40°C with AAMPS monomer (15% w/w), 0.1% (w/w AAMPS) initiator mixture of azobisisobutyronitrile (AIBN) and ammonium persulfate (APS) and 1% (w/w AAMPS) methylene bis acrylamide (MBA) in DI. Final mixture was poured into a glass mold then placed in a -17°C freezer for 16 h, subsequently thawing for 8 h at room temperature (RT). Resulting gel was polymerized in a convection oven ramping from 45°C to 55°C (R). The polymerized IPN was then subjected to one more freeze-thaw cycle and a subsequent polyethylene glycol (PEG, MW=400g/mol) immersion until equilibrium was reached, followed by unreacted monomer removal in saline by weighing until equilibrium. One group was tested as is (un-annealed) and another group was annealed by placing in a bomb in PEG400 under Argon and annealed for one hour at 160°C subsequent to equilibrium vacuum drying. The gels were then rehydrated in saline. PVA-AAm IPNs and 15-0 PVA control gel were prepared with the same method as PVA-AAMPS. PVA-PEG gels were prepared by mixing 15% (w/w) PVA (MW=115,000) and 28% ( $w_{PEG}/w_{H_2O} + w_{PEG}$ ) PEG in DI water at 90°C. The solution was molded and cooled down to room temperature for gelation for 24h. Two gel groups were prepared: One group was used in their 'as-gelled' form (AG). The other group was immersed in saline after gelation for PEG removal and was used in this 'dePEGed' form (DP). The AG gels were dried in a convection oven ramping from 25°C to 80°C with subsequent annealing in bomb under argon gas ramping from 80°C to 160°C and holding at 160°C for 1h. Annealed gels were rehydrated in saline until equilibrium. All gels were equilibrated in the respective lubricant at 40°C before testing. Relative coefficient of friction (RCOF) of the hydrogels was determined in the various lubricant solutions at 40°C while rubbing against an implant-quality finish cobalt-chromium surface using a custom annular fixture mounted on a controlled stress rheometer (AR-2000, TA Instruments Inc) with an inner radius of 1.44cm and a contact area of 1.42cm<sup>2</sup> at a constant angular velocity of 0.1rad/s. The RCOF between the hydrogel and the counterface was calculated using the method of Kavehpour and McKinley [3]. The equilibrium water content (EWC) of the hydrated gels in saline at 25°C and after equilibrium in each lubricant at 40°C was determined by measuring the weight loss during complete dehydration at 90°C. The total creep strain (TCS) of the non-annealed and annealed samples was determined on a custom made mechanical tester in saline at 40°C by applying a 100N load for 10h followed by a 10h relaxation period under 10N load.

### Results

PVA control gels showed the lowest EWC among all types of gels after equilibrium rehydration in saline at 25°C (Fig1). PVA-PEG, PVA-AAm

and PVA-AAMPS gels showed similar EWC values. EWC of all types of PVA hydrogels decreased after annealing (Fig 1).

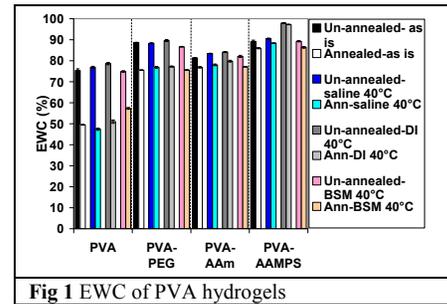


Fig 1 EWC of PVA hydrogels

contrast PVA-AAMPS gels showed a slight increase in EWC after equilibrating in DI at 40°C (Fig1). PVA control gels showed highest creep strength in their non annealed and annealed forms. Annealing increased the creep strength of all types of gels tested (Table 1). We found a strong positive correlation between EWC and TCS ( $\gamma_s = 0.6$ ). Incorporation of a hydrophilic polymer like acrylamide or AAMPS substantially decreased the RCOF of the PVA hydrogel which is likely related to the increase in the water uptake ability of these gels (Fig 2). Both PVA-AAm and PVA-AAMPS hydrogels showed lower RCOF values than PVA control and PVA-PEG hydrogels. Annealing increased the RCOF values in all types of gels. However this increase was less significant in PVA-AAm and PVA-AAMPS gels.

Sample	TCS (%)
PVA Control	60±5
PVA Annealed	19±5
PVA-PEG DP	88±3
PVA-PEG AG SRA	56±3
PVA-AAm Control	66±5
PVA-AAm Annealed	54±2
PVA-AAMPS Control	78±4
PVA-AAMPS Annealed	74±4

We postulate that addition of a functional group increases the water uptake ability thus the boundary film formation becomes more efficient which is believed to decrease friction in hydrogels [4]. We found a strong negative correlation between EWC and COF in saline, DI and BSM ( $\gamma_{sm} = -0.7, -0.9$  and  $-0.8$  respectively). Lubricant also has a strong effect on the RCOF of each gel. For every gel except for the AAMPS gels, the RCOF measured in saline was lowest, followed by DI, and the RCOF in bovine storage media was the highest. For the AAMPS gels, the RCOF was lowest in DI, followed closely by saline, and then the RCOF in

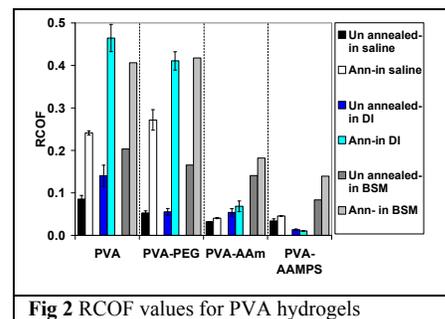


Fig 2 RCOF values for PVA hydrogels

SM was highest (Fig 2). This difference is likely due to ionic character of AAMPS.

### Conclusion

The addition of hydrophilic functional AAm and AAMPS in to PVA in the form of an IPN decreased the friction of the PVA gels significantly while maintaining the mechanical strength. The lubricant in which the gels were tested against a cobalt-chromium ring also has a strong influence on the RCOF. Lubricous and mechanically strong PVA-AAm and PVA-AAMPS are promising candidates as a load bearing synthetic articular cartilage.

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**References:** 1) Bodugoz-Senturk, H et al. Biomaterials, 2008, 29(2): 141-9. 2) Bodugoz-Senturk, H et al. 53rd Annual Meeting of the ORS, San Diego, 2007. Kavehpour, H. et al Tribology Letters, 2004, 17(2): 327-335.4) Yasunari, I et al, Wear, 2005, 261(5-6): 500-504.