Effect of Irradiation on the Strength and Lubricity of PVA-PAA Hydrogels for Cartilage Repair

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Introduction: Repairing cartilage is an ongoing challenge due to the limited autonomous healing ability of cartilage, and the lack of long term intervention strategies. Therefore, there is a great need for engineered biomaterials for cartilage replacement therapy to delay further invasive treatments. Hydrogels have been explored for this purpose. Polyvinyl alcohol (PVA) hydrogels are one of the most studied hydrogels due to their biocompatibility, lubricity, and high water content [1]. However, PVA hydrogels are not mechanically strong enough in their unprocessed form to serve as a cartilage substitute [1, 2]. In our previous publications we have shown that the addition of Poly(acrylic acid) (PAA) to the PVA network, and their subsequent thermal annealing, resulted in a tough and highly lubricous hydrogel [1, 2]. In this study we have investigated the effect of sterilization on these PVA-PAA hydrogels. Sterilization is essential to prevent post-operative infection which can lead to implant rejection. Radiation sterilization is the method of choice for most medical implants. However, high-energy irradiation can change the physical properties of the hydrogels. The focus of this study is to quantify the physical changes that occur in PVA-PAA hydrogels after undergoing sterilization with varying gamma irradiation doses and in different irradiation media.

Materials and Methods: PVA-PAA hydrogels were prepared by dissolving PVA (MW = 115,000g/mol, Scientific Polymer Products) and PAA (MW = 200,000g/mol, Polysciences) in a 25wt% 19:1 ratio, respectively, in deionized water (DI) at 90°C (Fig1). The solution was subjected to a freeze-thaw cycle, dehydrated, annealed, and hydrated in DI. A 25% PVA hydrogel was prepared as a control. Irradiation doses of 25, 50, 100, or 150kGy of gamma irradiation were applied to the hydrogels in an aqueous 50% PEG400 solution. PVA hydrogels were also irradiated in DI water to 25kGy as a control. Post-irradiation, the hydrogels were equilibrated in DI. All reported percentages were calculated relative to the final solution weight. The Equilibrium Water Content (EWC) was quantified using a Thermogravimetric Analyzer (TGA). Creep was assessed with custom built creep testers and were loaded at 0.5MPa for 10hours and then at 0.05MPa for 10hours. The total creep strain (TCS), the strain after ten hours of loading, was reported. Tensile strength was determined by pulling dogbone cut samples according to ASTMD638 standards at a rate of 20mm/min on a mechanical test frame (Insight, MTS). Relative Coefficient of Friction (rCOF) was measured using a stress controlled rheometer (AR-2000, TA Instruments). The rCOF was calculated with the Kavehpour and McKinley [3] method. Gel Content was calculated as the ratio of the dry, non-soluble component of the gel to the solid weight of the gel.

Results: As shown in Table1, irradiation did not significantly weaken the PVA-PAA hydrogel. All irradiated hydrogels showed similar break stress and strain values to the non-irradiated control. The moduli, however, of all irradiated groups were significantly lower than the non-irradiated hydrogels. 100kGy irradiated hydrogels exhibited lowest modulus value (4±2). While the irradiation did not affect the EWC significantly, an increase in rCOF was observed in irradiated hydrogels with no distinguishable correlation to the radiation dose (Table2).

Table1. Effect of irradiation dosage on mechanical properties PVA-PAA hydrogels.

Irradiation Dosage	Break Stress, (MPa)	Break Strain, (%)	Modulus, (MPa)
25kGy	14±1	310±41	8±2
50kGy	12±2	298±47	8±0.3
100kGy	11±0.2	303±58	4±2
150kGy	13±1	285±21	8±0.6
Non-Irradiated	15±1	333±39	13±3

Hydrogels irradiated with 25kGy and 50kGy had the highest (0.3±0.01), and lowest (0.1±0.05) rCOFs, respectively. All irradiated hydrogels, except the 25kGy irradiated hydrogels, had gel contents higher than that of the non-irradiated group.

Table2. Effect of irradiation on PVA-PAA hydrogels.

Irradiation Dose	rCOF	EWC, (%)	Gel Content, (%)	TCS, (%)
25kGy	0.3±0.01	50±2	64±3	18±6
50kGy	0.1±0.05	53±3	88±1	17±2
100kGy	0.2±0.08	58±4	89±1	21±2
150kGy	0.2±0.06	53±1	90±0.3	19±3
Non-Irradiated	0.06±0.01	58±1	73±1	14±5

The addition of PAA weakens hydrogels, regardless of irradiation media (Table3). However, PVA hydrogels have stronger mechanical properties when irradiated in DI; whereas PVA-PAA hydrogels are stronger when irradiated in PEG. PVA-PAA hydrogels irradiated in DI have the lowest rCOF (0.05±0.01) (Table 4). PVA hydrogels dissolved after boiling, while the PVA-PAA hydrogels exhibited high gel content regardless of irradiation media.

Table3. Effect of sterilization media on PVA-PAA hydrogels irradiated to 25kGy.

Irradiation Media	PVA/PAA	Break Stress (MPa)	Break Strain (%)	Modulus (MPa)
DI Water	19:0	20±0.5	402±16	34±4
	19:1	7±0.3	244 ±14	3 ±0.2
50% PEG400	19:0	17±0.4	426±18	21±3
	19:1	14±1	310±41	8±2

Discussion: Neither mechanical properties nor the water content of the PVA-PAA hydrogels changed significantly with irradiation dose. However, irradiation increased rCOF of PVA-PAA hydrogels. This is probably due to the radiation induced cross-linking as suggested by the gel content measurements (Table4). In both sterilization media, DI water and 50% PEG400, PVA hydrogels without PAA dissolved during high temperature boiling whereas PVA-PAA gels exhibited high gel content.

Table4. Effect of irradiation media on physical PVA-PAA hydrogels.

Irradiation Media	PVA/ PAA	rCOF	EWC (%)	Gel Content (%)	TCS (%)
DI Water	19:0	0.3±0.02	43±2	Dissolved	15±3
	19:1	0.05±0.01	69±1	87±1	24±2
50% PEG400	19:0	0.4±0.04	45±3	Dissolved	15±2
	19:1	0.3±0.01	50±2	64±3	18±6

References: [1] Bodugoz-Senturk H *et al*. Biomaterials. 2008; 29(2):141-9 [2] Bodugoz-Senturk H *et al*. Biomaterials. 2009; 30(4):589-596 [3] Kavehpour HP *et al.* Tribology Letters. 2004; 17(2):327-335