Tribological properties of PVA/PVP blend hydrogels against articular cartilage

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Abstract

This research investigated in-vitro tribological performance of the articulation of cartilage-on-polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) blend hydrogels using a custom-designed multi-directional wear rig. The hydrogels were prepared by repeated freezing-thawing cycles at different concentrations and PVA to PVP fractions at a given concentration. PVA/PVP blend hydrogels showed low coefficient of friction (COF) values (between 0.12±0.01 and 0.14±0.02) which were closer to the cartilage-on-cartilage articulation (0.03±0.01) compared to the cartilage-on-stainless steel articulation (0.46±0.06). The COF increased with increasing hydrogel concentration (p=0.03) and decreasing PVP content at a given concentration (p<0.05). The cartilage-on-hydrogel tests showed only the surface layers of the cartilage being removed (average volume loss of the condyles was 12.5±4.2 mm$^3$). However, the hydrogels were found to be worn/deformed. The hydrogels prepared at a higher concentration showed lower apparent volume loss. A strong correlation (R$^2$=0.94) was found between the COF and compressive moduli of the hydrogel groups, resulting from decreasing contact congruency. It was concluded that the hydrogels were promising as hemiarthroplasty materials, but that improved mechanical behaviour was required for clinical use.
Key Words: Cartilage, hemiarthroplasty, hydrogel, tribology, mechanical properties.

1. Introduction

The patellofemoral joint (PFJ) is composed of the patella and femur in the knee joint. The posterior surface of the patella and the surface of the distal femur are covered with articular cartilage. Articular cartilage functions to support and transmit the joint loads to underlying bones and to minimise the friction in the joint during daily activities. The PFJ is one of the most problematic articulating joints since the joint is subjected to high repetitive mechanical loads. Isolated PFJ osteoarthritis is common and affects from 9.2% up to 24% of the patients who have symptomatic knee arthritis, and affects all age groups [1, 2]. Isolated osteoarthritis does not involve other parts of the knee joint, so the PFJ is suitable for a partial joint replacement. In previous PFJ prostheses, the patellar component was made of ultra-high-molecular-weight-polyethylene (UHMWPE).

Unfortunately, these components may erode the cartilage on the femoral condyle in deep knee flexion, and so revision to a total knee arthroplasty may then be required [3, 4]. This study was based on the hypothesis that the condylar cartilage erosions may be reduced by use of a softer material on the patella, such as a hydrogel.

Polyvinyl alcohol (PVA) is one of the most tested hydrogels as a potential artificial articular cartilage [5-8]. PVA hydrogel can easily be processed and modified to have similar fluid content as articular cartilage (65–80% [9]). The 3D network structure of PVA has pores similar to the native cartilage [10-12], and PVA is hydrophilic and produces low frictional behaviour [13-15]. When loads are applied on PVA during an articulation, water within its porous structure is squeezed out to the contact area, resulting in the loads being mostly supported by the fluid phase and so low friction is achieved [11]. Kobayashi et al. [16] observed no breakage or wear of a PVA meniscus 2 years post implantation in rabbits. PVA has good biocompatibility in in-vivo experiments [17, 18]: Oka et al. [18] found no
inflammation or degenerative changes of tissues around implanted PVA plugs in rabbits. Stammen et al. [6] showed that the compressive modulus of PVA is strain rate and magnitude dependent and the modulus can be varied between 1 to 18 MPa, which is in the range of the modulus of articular cartilage. Baker et al. [19] reported mechanical properties such as compressive modulus and tensile modulus to be similar to the native articular cartilage. PVA hydrogel has been implanted to replace focal cartilage defects, and a 5 to 8 years follow-up showed improvement of knee function and reduction of pain [20].

Polyvinyl pyrrolidone (PVP) is also hydrophilic and biocompatible [11, 21, 22]. PVA/PVP blend hydrogels have been widely researched as a cartilage replacement material [23, 24]. Incorporating small amounts of PVP (0.5–5%) molecules to PVA improves polymer network stability through inter-chain hydrogen bonding between PVA hydroxyl groups and PVP carbonyl groups [24]. This increases the crystallinity and decreases the degradation of PVA hydrogels [24], and makes the compound surface smoother [25]. Ma et al. [26, 27] found reduced COF as PVP was added to PVA hydrogels when testing stainless steel balls on PVA/PVP hydrogels. Katta et al. [28] articulated cobalt-chromium pins against PVA/PVP blend hydrogels and found an average COF of 0.10 with bovine serum lubricant and as low as 0.04 for synovial fluid lubricant. In the same study, they also observed significantly lower wear as hydrogels were prepared with higher polymer content. The mechanical properties of PVA/PVP hydrogels can be approximated to mimic the articular cartilage by varying a number of parameters such as the concentration of the polymer content [29], number of freeze-thawing cycles [30], thawing rate [31], PVA molecular weight [32] and degree of polymerization [10].

Swelling and mechanical (i.e., compression, tension, and shear) properties of PVA/PVP hydrogels have been characterised [6, 11, 29, 30]. For instance, Holloway et al. [33] found higher compressive modulus and larger pore size with increasing number of freeze-thaw cycles. Also, compression tests on PVA/PVP hydrogels show a non-linear stress versus strain behaviour [23].
This study investigates whether PVA/PVP blend hydrogels will be useful in PFJ prostheses, which may also include their use in hemiarthroplasty, where they bear against articular cartilage. In the present study, PVA/PVP blend hydrogels (having a moderate amount of PVP content) were synthesised by a repeated freezing-thawing method. The primary objective of this investigation was to determine the effects of hydrogel concentration and PVP content at a given concentration on the tribological and mechanical properties. The effect of the degree of cross-shear on the surface damage of the PVA/PVP hydrogels was also evaluated.

2. Materials and methods

2.1. Cartilage specimen preparation

Within 6 h of slaughtering, adult ovine rear legs (18–24 months) were obtained from a local abattoir. Both left and right legs and medial and lateral condyles were used. The stifle joint was opened by removing its ligaments, tendons and capsule using a surgical scalpel and forceps. The medial and lateral condyles were cut from the femur using a hacksaw, and split apart to form a pair of specimens. The cartilage was kept hydrated with PBS during the extraction process. Each condyle was then cut to a width 11–15 mm, length 21–25 mm, and depth 13–15 mm using a hand saw. The condyle specimen was potted in a customised condyle holder using PMMA bone cement [34] (Figure 1a). The curved geometry of the part-spherical condyles inherently caused a more even contact stress distribution and enabled us to reduce the risks related to cartilage pin misalignment and lubricant starvation.
Experiments were also carried out in which femoral condyles were articulated against flat bovine cartilage plates (labelled as cartilage) to simulate a cartilage-on-cartilage negative control group to verify and compare with past literature [35-38]. The cartilage plates (width 13–15 mm, length 23–25 mm, and depth 6–8 mm) including a 3–5 mm thickness of subchondral bone were obtained from bovine patellofemoral joints. Tests of femoral condyles on surgical grade stainless steel discs (labelled as SS316L) were performed as the positive control group. The discs (diameter 38 mm, thickness 3 mm) were polished to an average surface roughness of 0.01 µm.

2.2. PVA/PVP blend hydrogel synthesis

PVA (>99% hydrolyzed) with a molecular weight of 89,000–98,000 g/mol and poly (vinyl pyrrolidone) (PVP) with a molecular weight of 40,000 g/mol were obtained from Sigma-Aldrich Ltd., Dorset, UK. 30 or 35 wt. % solutions were prepared to approximate the fluid content [9] and compressive modulus of cartilage. Isotonic saline [6, 26] was used to prevent osmotic imbalances between hydrogels and surrounding tissues [39, 40]. Polymer solutions were composed of 100 wt.% PVA, or 99 wt.% PVA and 1 wt.% PVP, or 95 wt.% PVA and 5 wt.% PVP. The hydrogels tested at different concentrations and contents are summarised in Table 1.
Table 1 Summary of tested hydrogels synthesised at different concentrations and contents

<table>
<thead>
<tr>
<th>Conc.</th>
<th>100% PVA</th>
<th>99% PVA and 1% PVP</th>
<th>95% PVA and 5% PVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>30%_100-0</td>
<td>30%_99-1</td>
<td>30%_95-5</td>
</tr>
<tr>
<td>35%</td>
<td></td>
<td></td>
<td>35%_95-5</td>
</tr>
</tbody>
</table>

The mixed solvent was sealed in a container and autoclaved at a temperature of 121 °C at a pressure of 1.05 bar for approx. 70 min until the mixed solvent became a viscous slurry. The aqueous solution was then poured into custom-made moulds (made of Perspex®: poly methylmethacrylate) to make discs 37 mm diameter and 3.3 mm thick. The cast solution was left at room temperature for at least two hours to increase solution uniformity. To induce physical crosslinking, the solution was then subjected to 20 h of freezing at –25 °C and 4 h of thawing at room temperature, which was repeated 10 cycles; a pilot study had found that this was the optimum protocol to establish maximum stiffness. The last 4 cycles were carried out outside of the mould by removing the solution from the mould to avoid constraining and damaging the material.

2.3. Pin-on-disc friction and wear test

The cartilage friction and wear experiments were carried out using a single-station multi-directional reciprocating motion pin-on-disc tester (Figure 2). The tester was designed to run long-term in-vitro wear and friction models, producing accurate measurements under physiological pressures and motions which had been calculated to be similar to those acting on the PFJ.
The friction force was detected using four strain gauges (Stock 632-168; RS Components Ltd., Northants, UK) attached to a u-shaped component and wired into a full Wheatstone bridge circuit. The gauges were attached to a thin area, to increase bending strains caused by the friction force (Figure 2). The voltage generated by the load cell was transferred through an analogue-to-digital converter and logged using a data acquisition system (MADAQ 40, Fylde Electronic Laboratories Ltd., UK). The output voltage \( V \) was converted into the friction force \( F \) using a known calibration factor \( F=4.4675V \) according to a linear regression analysis. A strong correlation \( R = 0.9995 \) was found between the output voltage and the frictional force. The friction force was then used to quantify the COF, which was defined as the ratio of friction force to normal compressive load.

Prior to testing, the hydrogel discs were fully hydrated by soaking in deionised water at least for 48 h. Test specimens were adhered on stainless steel discs using cyanoacrylate glue (Figure 1b) and then fixed in the test container.

During testing the rotary motion produced by a DC motor (Model RCM1–C–23L20–C–RT3; Reliance Precision Limited, UK) was transferred through a crank and slider mechanism to give \( \pm 12.5 \text{ mm} \)
horizontal reciprocating motion of the test container. Simultaneously, the container was rotated ±15° to produce cross–shear using a rack and pinion gear mechanism. Condylar specimens were mounted to the u-shaped component, which was stationary during testing. A shaft was screwed to the u-shape component, which could only move in a vertical axis through a plain bearing and could not rotate. A dead weight of 20 N was placed on the shaft to load the condyle specimen. This gave a contact pressure of 0.58±0.09 MPa for the hydrogel groups, 0.95±0.16 MPa for the negative control group, and 1.41±0.21 MPa for the positive control group, measured using extra-low-pressure (4LW) sensitive Fujifilm (Fuji Photo Film Co. Ltd., Tokyo, Japan) as used in other studies such as [34, 43].

Each test lasted 15 h at a frequency of 1 Hz. 30% (v/v) bovine calf serum (BCS) was used as the lubricant, which was kept at 37±1 °C throughout testing. The BCS volume (10–12 ml) and its protein content (20 g/L) were kept constant over testing by continuously replacing evaporated test lubricant water with fresh deionised water using a syringe driver.

**Table 2 Test conditions used for testing in pin-on-disc tester**

<table>
<thead>
<tr>
<th>Test specimens</th>
<th>Upper: ovine condyle Lower: hydrogel disc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding distance</td>
<td>25 mm</td>
</tr>
<tr>
<td>Sliding velocity</td>
<td>0–40 mm/sec (mean: 25 mm/sec)</td>
</tr>
<tr>
<td>Applied load, static</td>
<td>20 N</td>
</tr>
<tr>
<td>Frequency</td>
<td>1 Hz</td>
</tr>
<tr>
<td>Duration</td>
<td>15 h (54000 cycles)</td>
</tr>
<tr>
<td>Cross-shear (CS) angle</td>
<td>±15°</td>
</tr>
<tr>
<td>Test lubricant</td>
<td>30% BCS in DI water</td>
</tr>
<tr>
<td>Test temperature</td>
<td>37±1°C</td>
</tr>
</tbody>
</table>
2.4. Cartilage deformation

Condyles were rehydrated in PBS for 1 h after wear testing. This allowed any water exudation due to loading to return to the cartilage, and therefore the cartilage to equilibrate. After recovery, each condyle was replicated in a custom-designed jig (see Figure 3a) using Microset 101RF fluid compound (Microset Products Ltd., Leicestershire, UK). This replica rather than the condyle was used for cartilage deformation investigations to avoid measurement inaccuracy due to cartilage dehydration [34, 43].

Figure 3 Steps of the method to measure cartilage volume loss: (a) the replica of a worn condyle; (b) scanning the replica in the Talysurf; (c) true and predicted curves obtained using MATLAB. Note that the trace shows a positive control, where the cartilage covered femoral condyle was worn severely against a stainless steel counterface.

A Form Talysurf Series 2 (Taylor Hobson, UK) was used to assess deformation of the condyles and estimate volume change by scanning the replica (Figure 3b). The stylus tip traced a 20 mm length at 0.5 mm/sec. Approximately 10–15 traces (depending on the scar size) with a 0.5-mm gap between each trace [43] were scanned across each replica. A customised MATLAB script was written to predict a curve-fit (predicted curve) based on the unworn surface on either side of the scanned...
curve (true curve) (Figure 3c) [38]. The program highlighted the damaged area and this was used to calculate the wear volume on a slice-by-slice basis.

### 2.5. Hydrogel deformation

PVA/PVP hydrogels were left in deionised water for 24 h for recovery following wear testing, and then replicated in a customised jig using the Microset fluid compound (Figure 4a). The Talysurf was used to predict hydrogel volume change (Figure 4b). 11 traces (12 mm length) with a 2-mm gap were scanned at 0.5 mm/sec. A MATLAB script was written to predict a straight line (predicted line) based on the unworn surfaces on either side of the contact region (Figure 4c) and to calculate the damaged area and ultimately the wear volume on a slice-by-slice basis.

![Figure 4 Steps of the method to measure hydrogel volume loss: (a) the replica of a worn hydrogel disc; (b) scanning the replica; (c) original data and predicted line obtained using MATLAB.](image)

### 2.6. Surface characterisation

White Light Interferometry (WLI) was used to assess the surface roughness parameters and topographies of the hydrogel, cartilage, and stainless steel specimens before and after wear testing. WLI images were obtained using a Wyko, NT9100, (Veeco Instruments, Inc.) with a 20X magnification objective. Five separate measurements per sample were taken on each surface, and these
measurements were averaged to calculate the mean surface roughness $R_a$. Before imaging, cartilage specimens were gently dried using lint-free tissue to remove fluid from the surface and imaged within 5 min to minimise dehydration [42]. Replicas of the hydrogel discs were imaged due to their transparency and water content, which reduced accuracy. The accuracy of the replicating method was validated by comparing surface roughness parameters obtained from an aluminium part ($R_a$ 424±48 nm) and its replica ($R_a$ 451±47 nm).

2.7. Measurement of hydrogel compressive properties

A micromechanical material testing system (Mach-1™, Biomomentum Inc., Canada), with a 70 N load cell, was used to investigate tangent modulus and stress relaxation of hydrogel discs 10.5 mm diameter and 5.5 mm high in unconfined compression between two impermeable platens. A preload of 0.1 N was applied to ensure full contact. Tests were performed in saline solution at 37°C for 5 independent samples. Each sample was compressed to 9% strain at a strain rate of 16.67% per second to quantify the compressive tangent modulus at strains of 2, 4, 6, 8, and 9%. The 9% strain was held constant for 5 min to investigate the stress relaxation behaviour.

2.8. Statistical analysis

All results which are displayed in graphs are presented as the mean (n=6) ± 95% confidence limits (CLs). Data were analysed using an independent t-test to compare individual differences between groups and a paired-sample t-test to compare individual differences within the same group. A one-way ANOVA was used to compare differences between more than two groups.
3. Results

3.1. Coefficient of friction

All hydrogels showed similar friction behaviour, with COF in range 0.12-0.15 (Figure 5). In comparison, the positive controls (stainless steel counterface) showed COF approx. 0.45 midway through the tests, and the COF of the negative controls (articular cartilage counterface) remained at approx. 0.03 throughout the tests.

Figure 5 COF over 15 h for hydrogels. Data presented as mean (n=6) ± 95% CLs. The upper graph has greater range to show the higher and lower COF from the two control groups. The lower graph shows the data from the PVA/PVP specimens at higher magnification.
Figure 6 shows the average COF between 0–15 h of wear testing for control and hydrogel groups. The COF of the hydrogels was significantly lower than the positive control group and greater than the negative control group ($p<0.05$). Among the hydrogel groups, increasing the PVP content from 30 to 35% significantly increased the COF ($p=0.03$). Among the 30% hydrogels, there was a tendency (n.s.) for reducing COF with increasing PVP content.

![Figure 6 Average COF between 0–15 h of wear testing. Data presented as mean (n=6) ± 95% CLs.](image)

### 3.2. Cartilage deformation

Following wear testing articular cartilage specimens were visually inspected. For the negative control group, neither surface damage nor wear was observed on either the ovine condyles or the bovine plates. The cartilage-on-hydrogel tests showed only the surface layers of the condyles being removed. However, severe wear was found on all condyles from the positive control group after 15 h testing, with an average volume loss of $12.5±4.2$ mm$^3$.

### 3.3. Hydrogel deformation
On visual inspection, no surface damage was observed on the stainless steel discs or the cartilage plates. Different levels of hydrogel volume loss were detected, depending on the test group, using the Talysurf method (Figure 7). The volume loss from the 35%_95-5 group (19.0 ± 5.7 mm³) was lower than the other three groups, but only significantly lower than the 30%_100-0 group (29.8 ± 4.7 mm³) \((p=0.01)\). No correlation \((R^2 = 0.38)\) was found between the COF and the volume of cartilage lost during testing.

![Figure 7 Volume loss measurements for hydrogels after 15 h wear testing. Data presented as mean (n=6) ± 95% CLs.](image)

### 3.4. Surface characterisation

Figure 8 shows the \(R_a\) of the articular cartilage before and after wear testing. No significant difference was reported between the groups before testing \((p>0.05)\). There was a significant increase after testing for all tested groups \((p<0.05)\) except for the negative control group \((p=0.44)\). The largest increase was found in the positive control group (from 406 ± 48 nm to 1892 ± 452 nm).
For the negative control group, cartilage surface topography did not change after testing (Figures 9a and 9b), with several shallow humps and pits. The surface layer of the condyles from hydrogel groups was removed, and surface fibrillation along the sliding direction was found (Figure 9c). Due to excessive tangential loading, an amount of cartilage material (extracellular matrix) was removed from the contact zone, resulting in deeper pits (Figure 9d) in the positive control group.
Figure 9 Cartilage surface topographies obtained before testing (a) and after testing for (b) the negative control group, (c) the hydrogel groups and (d) the positive control group.
Figure 10 shows the $R_a$ of the hydrogels. Measurements were obtained from non-worn and worn surfaces of the replicas of the hydrogel specimens after wear testing. No significant difference was found between the non-worn surfaces of the tested groups or between the worn surfaces of the tested groups ($p>0.05$). The worn areas were significantly rougher than the non-worn areas ($p<0.05$).

![Average surface roughness (nm)](chart)

Figure 10 $R_a$ of hydrogel, obtained from non-worn and worn surfaces of the replicas of the hydrogels following testing. Data presented as mean (n=6) ± 95% CLs.
Figure 11a shows a photograph of a replica hydrogel wear scar. Area 5 was at the mid-stroke position, and areas 3 and 7 were at the ends of the stroke. The surface topography observed in area 2 (The ‘creep area’ is that area where the surface was below the surrounding (originally flat) surface, due to creep, but which was outside of the wear zone) was similar to those in area 1 (non-worn surface) (Figure 11 b1). Due to the removal of hydrogel matrix from the surface, pits and scratches along the reciprocating direction were found within the scar. The surface damage in areas 4 and 6 (Figure 11 b4) was greater than that at the ends (Figure 11 b3) and in the middle of the stroke (Figure 11 b5). A larger deformation was found where the combination of sliding distance and maximum cross-shear degree occurred, at areas 4 and 6.

Figure 11 (a) Photograph of a wear scar on a hydrogel replica; and (b) surface topographies obtained from different locations on the scar: b1 = area 1 in (a); b3 = area 3; b4 = area 4; b5 = area 5.
3.5. Hydrogel compressive behaviour

A similar stress versus strain curve was observed in all hydrogel groups, typically as shown in Figure 12.

![Graph showing compressive stress versus strain for hydrogels.](image)

*Figure 12 A typical stress-strain curve for hydrogels.*
Compression modulus increased with strain magnitude for all tested groups. The tangent modulus of the hydrogels varied between 0.17±0.02 MPa and 0.64±0.01 MPa, depending on the strain magnitude, the hydrogel concentration and the amount of PVP at a given concentration (Figure 13). The 35% hydrogel concentration had a significantly higher compression modulus than any of the 30% groups at any given strain magnitude (p<0.05). Increasing the PVP content caused a decrease in the compression modulus.

![Figure 13 Compressive tangent modulus at different strain magnitudes for hydrogels. Data presented as mean (n=5) ± 95% CLs.](image-url)
There was a strong correlation ($R^2=0.94$) between the COF and compression modulus (Figure 14).

![Chart showing the correlation between COF and compression modulus](chart.png)

Figure 14 A strong correlation ($R^2 = 0.94$) was found between the COF and compression modulus. 1: 30%_100-0; 2: 30%_99-1; 3: 30%_95-5; 4: 35%_95-5
The strain was held constant at 16.67% for 5 min to investigate the stress relaxation behaviour of hydrogels. The stress relaxation was in the range 15% to 17% for all tested groups (Figure 15).

![Stress relaxation curve for hydrogels at 16.67% strain. Data presented as mean (n=5) ± 95% CLs.](image)

4. Discussion

This study examined the tribology and mechanical behaviour of PVA/PVP blend hydrogels when bearing against a natural articular cartilage counterface, as would be encountered after hemiarthroplasty of a joint. The hydrogels were synthesised by repeated freezing-thawing cycles at different hydrogel concentration and content, and were formed with a comparable compressive modulus to articular cartilage [19]. Negative (cartilage-on-cartilage) and positive (cartilage-on-stainless steel) control groups were tested and compared to hydrogels. It was found that the hydrogel samples gave friction and wear behaviour that was between the extremes of the control groups. The rate of hydrogel wear/deformation meant that they were insufficiently robust to be used as human joint replacement bearings.
The negative control group (cartilage-on-cartilage) showed a constant COF of 0.03±0.01. The cartilage plates maintained biphasic load support because of their low permeability [44] and rehydration of the interstitial fluid during the unloaded phase [45]. Therefore, the intrinsic biphasic lubrication of the cartilage plates supported most of the loading during the articulation, resulting in low and constant friction outcomes; this was possible because the contact patch on the reciprocating cartilage plate was only under load intermittently, as it passed through the contact area under the stationary femoral condyle, and so the cartilage plate was able to remain hydrated and thus maintain the low-friction lubrication regime. The positive control group (cartilage-on-stainless steel) produced an increase in friction over the initial 90 min due to its biphasic nature. As the articular cartilage of the femoral condyle was under static loading for a long period, interstitial fluid was progressively exuded from the cartilage. Therefore, the load support fraction of the solid phase (the extracellular matrix) increased with time and so did the COF [46]. On the other hand, hydrogels showed constant friction values (ranging from 0.12±0.01 to 0.14±0.02) which were between those of the negative and the positive control groups, in agreement with previous studies [36, 37].

The COF decreased with increasing PVP content, in agreement with the literature [25, 26]. Increasing PVP content (and thus amide groups) results in an increase in equilibrium water content of the hydrogels, which improves the lubrication [26]. Guo et al. [47] studied tribological characteristics of PVP as a lubricant additive for artificial knee joints, and found that adding PVP to the test lubricants decreased wear and friction.

All tested hydrogels showed a non-linear stress versus strain behaviour under unconfined compression (Figure 12). The stiffness increased with increasing strain for all tested groups, as reported previously [6, 11, 23]. A significant increase in the compressive modulus was found at higher hydrogel concentration, as in previous studies [6, 29, 30, 33]. Increasing PVP content at a given concentration resulted in a decrease in compressive modulus.
A strong correlation ($R^2=0.94$) was found between the COF and compressive modulus among the hydrogel groups (Figure 14). Increasing compressive modulus resulted in decreasing contact congruency and an increase in the COF. Lower COF in more congruent bearings are associated with an increase in micro-elastohydrodynamic lubrication in the contact area due to the elastic deformation of the bearings [38, 48-50]. Congruent contact also lengthens the time constant for loss of fluid pressurization under constant loading in porous structures [51], resulting in a decrease in COF.

Upon visual inspection there was no damage on the condyles from the negative (bearing against articular cartilage) control group, but severe damage in the condyles from the positive control group (bearing against polished stainless steel). It is promising that the condyle-on-hydrogel tests showed only the surface layers of the condyles being removed, which was not detectable using the Talysurf. In these tests, the contact area on the condyle was fixed, whereas in life it moves by a combination of rolling and sliding, which would reduce the severity of wear conditions at the spot tested using the reciprocating rig used in the present study.

Although the condyles were almost intact, the hydrogels had been deformed. Hydrogels prepared at a higher concentration (35% wt.) showed lower volume loss, as reported previously [28, 52, 53]. Katta et al. [28] postulated that a higher concentration hydrogel had a higher degree of cross-linking or crystallization, resulting in an increased mechanical strength and resistance to wear. Freeman et al. [53] also observed a decrease in wear with increasing crosslink density for polyHEMA hydrogels. It could also be speculated that some of the reduction in deformation with increased hydrogel concentration resulted from reduced creep.

There was little correlation ($R^2=0.38$) between volume loss and COF, which indicates that in some cases friction and wear are unrelated to each other. Katta et al. [28] also found little relationship between wear and COF for PVA/PVP hydrogels. It could be speculated that the interactions between the several changing variables cancelled each other, such as (for example) increasing conformity due...
to creep versus increasing surface roughness. In order to learn more about this evolution, it would be interesting to examine the surfaces at multiple time points during the tests, however, that might then influence the evolution of the behavior of the cartilage counterface.

A significant increase was found in articular cartilage surface roughness ($R_a$) after testing for all tested groups ($p<0.05$) except the negative control group ($p=0.44$). The largest increase was found for the positive control group. There was a significant difference of roughness between non-worn and worn areas of all tested hydrogels. Different levels of surface damage were found along the wear track on the hydrogels because the pin-on-disc tester produced different degrees of cross-shear over a stroke; the surface damage was highest where the cross-shear was largest (Figure 11).

In a pilot study, a 30% hydrogel with 75% PVA and 25% PVP (30%_75-25) was also articulated on a condyle. The COF was 0.08 which was considerably lower than that obtained from the other hydrogel groups. However, after wear testing, upon visual inspection the hydrogel disc was found to be torn along the sliding direction. The volume loss of the hydrogel disc (56.20 mm$^3$) was also considerably greater than that of the 4 tested groups (between 19 - 30 mm$^3$). This suggested a decrease in mechanical strength with increasing PVP content, due to reduced hydrogel network stability [24], and so this formulation was not studied further.

Only static loads were applied to the condyles in our customised reciprocating rig although the loads experienced in synovial joints are dynamic. Nevertheless, all specimens were tested identically, and thus any differences were expected to extend to other test methods. Moreover, the condyles were exposed to continuous static loading, which is a worst case scenario, useful for short-term screening tests as in the present study.

During wear testing, contact pressures decreased due to increasing contact areas, which was associated with the creep of the condyles and hydrogels as well as the removal of the cartilage matrix from the condyles. In future, tests performed using cartilage pins rather than condyles could
provide constant contact pressures during testing, although alignment and edge loading effects would be challenging.

Obvious creep on hydrogel specimens was observed after 15 h condyle-on-hydrogel static loading with no motion. Shi et al. [11] also found permanent deformation of PVA/PVP hydrogels under static loading. These studies suggested that in our test configuration a hydrogel disc’s apparent volume loss was the combination of linear wear and creep. However, creep amount could not be separately calculated and then subtracted from its total volume loss, to infer the linear wear. Thus, a future static creep study may be informative.

5. Conclusion

All tested hydrogels showed COF less than the positive control group and near the negative control group. Among the hydrogel groups, 30%_95-S showed the lowest COF and had a relatively higher PVP content. The condyles articulated against stainless steel discs were severely deformed after wear testing. In contrast, the condyles from the hydrogel groups were almost intact (only the surface layer was removed and there was no detectable volume loss). Because PVA/PVP hydrogels produced low COF against articular cartilage and did not damage the articulating cartilage counterface, they are attractive as cartilage mimicking materials.

However, none of the tested hydrogels could achieve the required long-term tolerance to loading, owing to the combination of wear and creep. If these hydrogels are to be used as part of a joint replacement, they require further development to enhance their mechanical strength, for instance using a double-network hydrogel technique [54]. Moreover, cartilage tissue is porous with a very small effective pore size in the range of 2.0–6.5 nm [55] whilst PVA/PVP hydrogel pore sizes are much larger and reported to be in the range of micrometres [33]. Parkes et al. [42] reported an improved mechanical performance of hydrogel scaffolds with decreasing pore size since small pore
size reduces the permeability of the material and thus increases the fluid load support [56]. Smaller pores also act to distribute stress more evenly and stop possible crack propagation [57].

Therefore, an overall conclusion is that, while the hydrogels had low COF and caused very little damage to a natural articular cartilage counterface, the mechanical behaviour of the formulations tested in this study requires upgrading if these materials are to be considered more seriously than in the present screening tests for long-term human joint hemiarthroplasty.

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References


