Mechanical and tribological characterisations of PEG-based hydrogel coatings on XLPE surfaces

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A R T I C L E I N F O

A B S T R A C T

Hydrophilic hydrogel coatings can impart enhanced tribological and antifouling properties to biomedical device surfaces. The influence of crosslinking on the elastic moduli of poly (ethylene glycol) (PEG) hydrogels is well established, however, the effect of crosslinking on the ability of the hydrogels to form coatings on crosslinked polyethylene (XLPE) substrates is not fully understood, nor are the mechanics and tribological performance of the resultant hydrogel coated substrates. PEG hydrogels of four different crosslinking levels (5, 7.5, 10 and 12.5% crosslinker concentrations) were deposited onto XLPE substrates. Crosslinked matched hydrogel plugs were also manufactured for mechanical analysis. The wear performance and friction evolution of coated pins were assessed against sterilised cobalt chromium discs at a contact pressure of 0.08 MPa under an elliptical orbital motion. The indentation results showed an increase in the elastic modulus with increasing crosslinker concentration, which was augmented further by gamma sterilisation treatment. Hydrogel coated pins exhibited reduced friction levels compared to uncoated pins, and confocal imaging in conjuction with the roughness monitoring indicated that the coatings protected the asperities from being removed. The friction values increased as the tests progressed, in line with the coverage of the hydrogel coating decreasing and forming a hybrid XLPE/gel vs CoCr contact. The 10% cross-linker hydrogel coating produced the lowest friction and wear of all the coatings tested.

1. Introduction

The surface modification of biomedical devices using hydrophilic hydrogel coatings can enhance surface wettability and biocompatibility, providing superior lubricity and wear resistance, as well as antimicrobial and antifouling properties [1–6]. The ability to adjust the hydrogel composition and microstructures as well as the deposition method means the physical and mechanical properties of the coating can be customised to the specific clinical needs [7–9].

The mechanical properties of soft hydrogels can be tailored by controlling the degree of crosslinking. The crosslinker to monomer ratio is key to forming a homogeneously-structured crosslinked hydrogel coating with consistent mechanical properties, strong durability, and low-volume shrinkage [10]. It is well established that there is a linear relationship between the elastic modulus increase and increasing crosslinker concentration [11–13]. However, the crosslinker concentration also influences the time-dependent behaviour of the hydrogel

network, with a higher level of crosslinking resulting in a decrease of the viscous component in the viscoelastic materials as crosslinking prevents polymer chain movement. As the crosslinker concentration is decreased, the poroelastic contribution becomes more important than the visco-elastic contribution [14].

Crosslinked PEG-based hydrogel coatings have previously been generated on a number of substrate materials, with adhesion achieved through several coating methods, such as surface bridging, surface initiators, and the advanced hydrogel painting method [15–17]. For synthetic hydrogels, increased crosslinking density has been shown to reduce the wear depth by over 60% [18]. The most common cause of late-state failure of total joint replacement (TJR) is aseptic loosening which is often related to the release of wear particles from the softer polymeric component (e.g. ultrahigh molecular weight polyethylene (UHMWPE) acetabular cup surface) in the hard-on-soft TJR bearings. The wear resistance of crosslinked PEG-like coatings on UHMWPE can be improved by increasing the degree of crosslinking, evidenced by the

damage modes exhibited in nano-scratching tests [19]. Wear of hydrogels has been determined either by gravimetric methods [20–22], or the wear depth profile [18,19,23]. However, the above-mentioned methods have limitations on measuring thin layers on substrate surfaces (i.e. the coating thickness is comparable to the roughness of the substrate surface), as it is difficult to distinguish the wear volume of hydrogel coating alone from the wear volume of coating/substrate system.

Conflicting findings have been reported for the effect of crosslinking on the frictional behaviour of hydrogels. Colloid probe atomic force microscopy (AFM) measurements [24] have shown an increase in crosslinking results in a decrease in friction, while friction increased with polymer volume fraction [24,25]. It was thought that relatively high crosslinking resulted in boosted interstitial fluid pressure, enhancing the lubricity, and lower friction [26]. In contrast, other studies have found friction coefficients to increase with the degree of crosslinking degree due to the decrease of conformational freedom of the polymer chains [27,28]. This was attributed to the higher crosslink density leading to less swelling and a higher polymer segment density [29]. It is believed that the discrepancy in results are largely due to the variations in the physical or chemical properties of different hydrogels as well as the test configurations such as sliding speed, applied load and contact configurations [26,30,31]. Moreover, previous studies investigated the friction behaviours at the nano/microscale [27–29], and very few tend to assess both the long-term friction and wear behaviours of hydrogels [18,21,31,32]. Friction behaviour observed in macroscale testing may not be similar to that at the nano/microscale, and it can significantly change as the coated sample wear [30]. There have been a few investigations reporting on the correlations between the friction and wear of bulk hydrogel [18,21], but no studies have investigated this for thin hydrogel coatings.

This study aims to investigate the influence of cross-linking on the mechanical and tribological behaviours of PEG-based hydrogel coatings on polyethylene (XLPE) substrates at the macro scale. The friction and wear of coated pins against sterilised cobalt chromium discs were monitored to determine the optimum degree of cross-linking for reduction in friction and wear, and mechanisms are proposed for the observed behaviours.

2. Materials

The substrates used in this study were vitamin-E infused XLPE pins and cobalt chromium (CoCr) discs (Mathys Ltd. Bettlach, Switzerland). The CoCr discs had a diameter of 32 mm and were polished to have an average roughness (Ra) ≈0.01 µm as measured by an Intra Touch stylus surface profilometer (Taylor Hobson Ltd.). The CoCr discs were subjected to a passivation treatment with a solution of 30 wt% nitric acid at 25 °C for 1 h, and gamma irradiation sterilisation with the nominal dose of 25–42 kGy. The 9 mm diameter XLPE substrates were manufactured with a surface roughness Ra between 0.8 and 1 µm, as measured with a Proscan 2200 Profilometer (Scantron Industrial Products Ltd, Somerset, UK).

The XLPE substrates were coated with a PEG-based hydrogel coating using a patented protocol, based on an immersion deposition method after surface activation via plasma treatment and silanisation [33]. All the XLPE substrates were washed with distilled, de-ionized (DDI) water, dishwasher detergent (mixed with DDI water in a ratio of 2:1 v/v), DDI water again and finally ethanol. After drying the samples in an oven at 70 °C for 12 h, the surfaces were activated with a low-pressure plasma Nano Diener using 600 W for 10 mins under 0.3 mbar of O_2. The samples were then subjected to a silanisation process, where they were immersed in a solution of 2% silane 3-(trimethoxysilyl) propyl methacrylate (TMSPM) in absolute ethanol for 12 h, then rinsed in ethanol and placed in an oven at 70 °C for 6 h to dry.

After plasma activation and silanisation, aqueous solutions at 2% weight/volume were prepared, containing a mixture of poly [(ethylene glycol) methacrylate] (PEG-MA, Mn = 360 Da, Sigma-Aldrich Co.) as

monomer, and poly (ethylene glycol) dimethacrylate (PEG-DMA, Mn = 550 Da, Sigma-Aldrich Co.) as a cross-linking agent. The molar ratios of PEGMA:PEGDMA in the monomer mixture were 95:5, 92.5:7.5, 90:10 and 87.5:12.5. After adding the monomers in water, degassing of the solution with nitrogen was required. Then, 1% of solid content weight of ammonium persulfate (APS, Sigma-Aldrich Co.) with a molecular weight and purity of 228.20 g/mol and ≥99.99%, respectively, was added in the mixture as thermal initiator, and a 0.05 wt% of solid content of Rhodamine was also added to make the coating fluorescent.

Substrates were immersed in at least 1.5 mL of this mixture per cm² of surface to be coated and allowed to react at 70 °C over 24 h, the samples were then sonicated in DDI water twice for 5 mins and allowed to dry in a fume hood overnight. The control (uncoated) and coated XLPE pins were sterilised by gamma radiation with a nominal dose of 25–35 kGy.

To determine the effect of crosslinking level on the elastic modulus value, 20 wt% of PEG mixtures were prepared with 5, 7.5, 10, 12.5 wt% of the cross-linking agent PEG-DMA. PEG hydrogels were fabricated in phosphate buffered saline (PBS) in a climate chamber at 70 °C and 98% humidity for 2 h. Thermal free-radical polymerisation was initiated by APS. These hydrated PEG hydrogel plugs were 6–7 mm in diameter and ~2 mm thick.

3. Experimental methodologies

3.1. Nanoindentation of crosslinked matched hydrogel plugs

The nanoindentation tests were performed using a NanoTest Vantage system (MicroMaterials Ltd., Wrexham) with a soft contact protocol [12]. A spherical diamond tip with a 500 µm radius was used. The nanoindentation tests were run in a load-control method to a maximum load (between 10 and 25 µN) with a targeting indentation depth of 20 µm. The loading rate was set at 1 µN/s and 5 µN/s, and unloading rate at 5 µN/s, with a 120 s hold at maximum load. Two samples were tested for each hydrogel formulation and 60 indentations were acquired for each hydrogel formulation. During testing, the PEG hydrogels were fully immersed in PBS solution using a liquid cell setup. All tests were run in a temperature-controlled environment (20 ± 1 °C).

The elastic modulus of the PEG hydrogels was obtained using the Hertz model which is widely used for analysing the nanoindentation measurements of soft materials [34]. When using a spherical tip with a radius of R, the force-displacement data during the loading response are fitted to the Hertzian elastic loading response, as expressed in equation (1):

$$F = \frac{4}{3}E_r R^{1/2} d^{3/2} \tag{1}$$

where F is the applied load, d is the displacement. For soft materials, as the compliance of the indenter.

is much less than the compliance of the soft materials, the reduced modulus (also called the effective modulus) can be written as $E_r = E_s/(1-v_s^2)$, in which E_s and v_s denote the Young's modulus and Poisson's ratio, respectively. The values of the Poisson's ratio were not known for the hydrogels investigated here as they can vary with the level of cross-linking, and thus the E_r values will be reported in this study.

To identify if there is a statistically significant difference in two group comparisons, one-way ANOVA with Tukey's HSD post-hoc test was employed. Statistical significance was achieved when p-values were less than 0.05.

3.2. Hydrogel coating characterisation

The thickness and coverage of the PEG-based hydrogel coatings on the XLPE substrate were evaluated using an inverted laser scanning confocal microscopy (Leica SP8 AOBS, Leica, Cambridge, UK). The
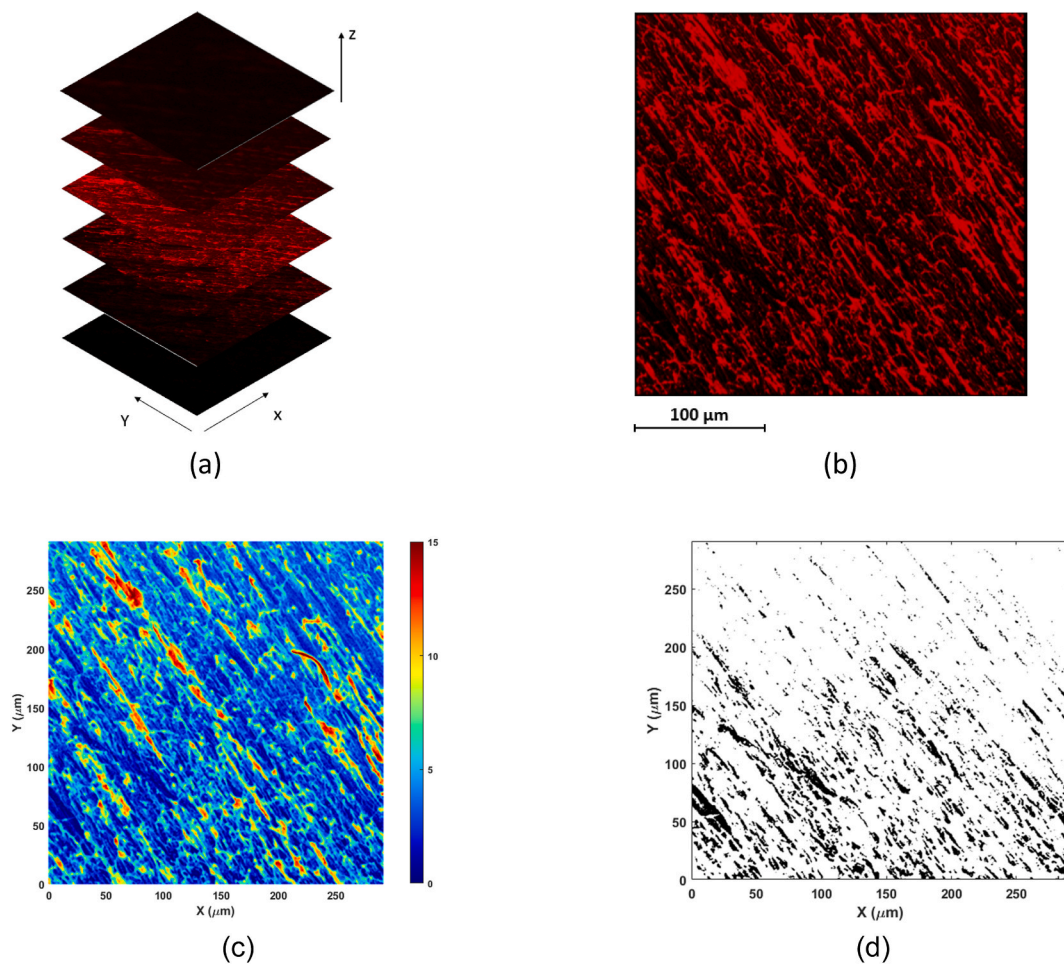
Fig. 1. The methodology of characterising the volumes and coverage of PEG hydrogel coatings using confocal image stacks: (a) confocal image z-stacks; (b) 2D confocal image of Rhodamine-stained hydrogel coating; (c) local thickness map; (d) hydrogel coating coverage (in white).

coatings were stained using Rhodamine Red fluorophores at a fluorophore to solid content ratio of 0.05:100 (mg/mg). Prior to confocal imaging, the coated XLPE samples were immersed in deionized water for 48 h to fully hydrate the hydrogels. During scanning, the samples were immersed in deionized water in a glass dish (ThermoFisher Scientific), to ensure the hydrogel coating was kept hydrating. The coatings were excited by a laser with a wavelength of 561 nm during imaging, which employed a 40 × magnification oil immersion objective. The image area was 291 μm × 291 μm, and z-stacks with a step size of 0.34 μm (Fig. 1a and b). Four measurements were taken on each pin (the number of pins n = 8) at different locations, both prior to testing and at each interval analysis.

The confocal image stacks were converted into binary images using the Otsu threshold method [35] in ImageJ. This threshold method proved an effective tool to determine the foreground objects (i.e. hydrogel coatings) from the background, by grouping all pixels into two colours (black and white), and then determining the average pixel value within each colour, then assigning the threshold value as the midpoint between the averages of the bright and dark pixels. After applying image binarization to the original confocal image stacks, the X and Y co-ordinates of each bright area within each stack were output, and then were converted into the thickness by accounting the number of slices (N) at each (X, Y) coordinate, i.e., thickness = 0.34*(N-1). The coverage was then determined from binary image of thickness maps, by dividing the pixel areas where the local thickness value was above zero to the scanning area (Fig. 1c and d). Finally, the volumes of hydrogel coatings were quantified by summing hydrogel local thickness in each pixel area
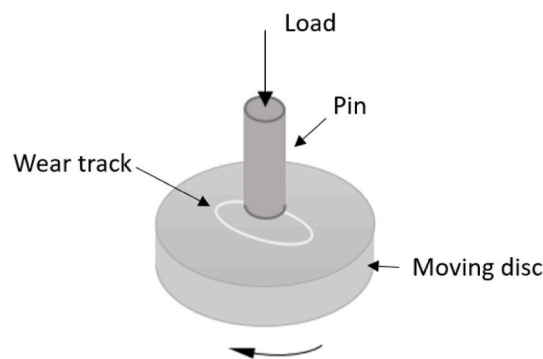

Fig. 2. Schematic illustration of pin-on-disc configuration: a static XLPE pin against a moving CoCr disc in orbital motion (10 mm major axis by 4 mm minor axis).

(0.32 μm^2), and the volumetric wear rate of hydrogel coating was reported as the total volume loss up to the present per unit load per unit meter, in the unit of mm^3/(Nm).

3.3. Wear testing

Each crosslinking level of coated XLPE pins and an uncoated control XLPE pin were tested using an 8-station pin-on-plate tribometer (TE-85 multi-station rig, Phoenix Tribology Ltd, UK) with the fixed XLPE pin
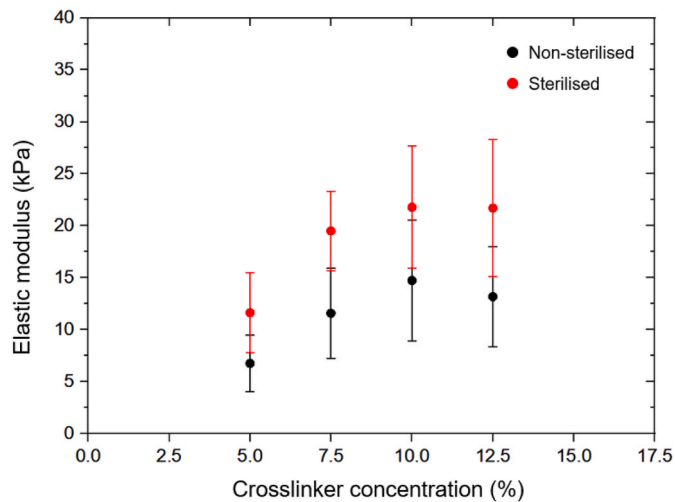
Fig. 3. Reduced moduli as a function of crosslinker PEGDMA concentrations for non-sterilised and sterilised PEG-based hydrogels.

loaded against a moving CoCr disc. The XLPE pins were loaded with a static load of 5.1 N (equivalent to a nominal pressure of 0.08 MPa) against CoCr discs, the tribometer produced in an elliptical orbital motion (Fig. 2) and were run for 200,000 cycles at 1 Hz. The elliptical sliding track had a 10-mm major axis and 4-mm minor axis. The lubricant used was a 25% (v/v) diluted solution of bovine calf serum (Sigma-Aldrich, Merck), with an average protein concentration of 20 g/L, and was delivered continuously to each bearing surface at room temperature by a computer controlled peristaltic pump. Prior to each wear test, the coated XLPE pins were hydrated in deionized water for 48 h prior to testing. The friction force was measured every 1000 cycles with high-speed friction force data collected at a frequency of 1 kHz for 5 s.

The wear tests were paused every 50,000 cycles to carry out interval analysis. During each interval analysis, the pin was removed from the tribometer, and then immersed in distilled water and ultrasonic cleaned three times for 10 mins, with the distilled water changed between each cleaning. Roughness measurements were performed on each pin using a Proscan 2200 non-contact profilometer with the measured length of 4.8 mm. A cut-off wavelength of 0.8 mm was employed, and 80 scan lines (individual 2D profiles) were performed across each pin. The pin was then immersed in distilled water with the wear surface against a 12 mm diameter of glass dish for the confocal microscopy analyses. The wear tests were repeated on separate eight sample pairs, and the average friction and wear rate with one standard deviation from eight repeated tests were reported for each hydrogel coating and uncoated pin.

3.4. Contact angle measurement

The wettability of uncoated XLPE and hydrogel coating surfaces was determined by measurement of the contact angle of a deionized water droplet on the uncoated/coated surfaces, using a Theta 200-Basic model of Biolin Scientific (serial number AAX100072). All tests were carried out at room temperature using the sessile drop method (static method) with a water drop volume of ~11 μl. The drop was allowed to settle for 3 s, then both left and right contact angles were measured for 5–8 s using the One Attension software. This software allows the baseline to be adjusted and calculates the average from right and left contact angles for every registered measurement. One measurement was performed on each sample (samples n = 8).
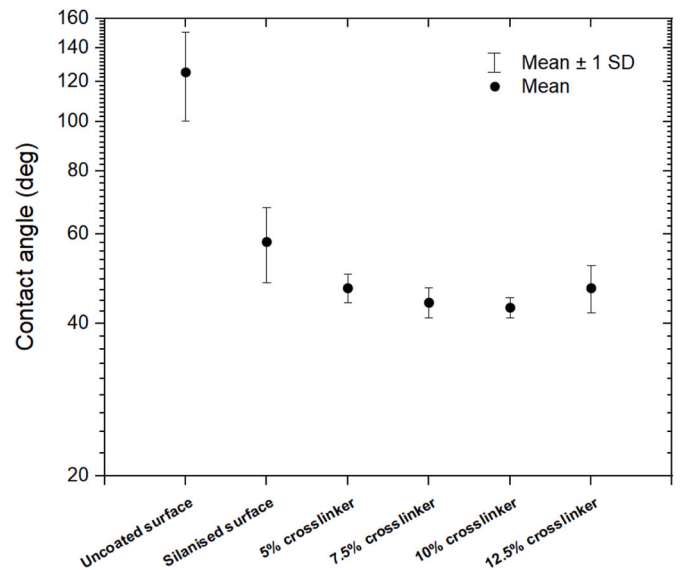

Fig. 4. Contact angle measurements for uncoated XLPE substrate surface, XLPE surface after silanisation process, and coated XLPE surfaces with a range of crosslinking levels.
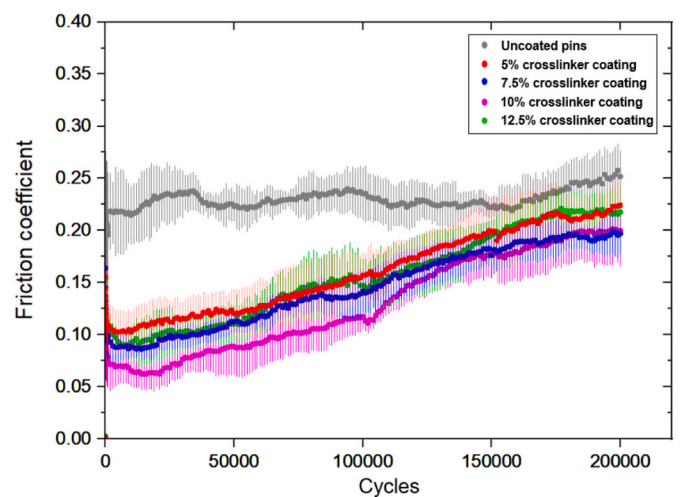

Fig. 5. The friction behaviours for uncoated XLPE pins and PEG hydrogel coated pins with various crosslinking levels against CoCr discs during 200,000 cycles of wear tests.

4. Results

4.1. Elastic moduli related with crosslinking and sterilisation

The average elastic modulus values of the PEG-based hydrogels increased with increasing concentrations of cross-linker PEGDMA between 5% and 10% for both non-sterilised and sterilised PEG hydrogels (Fig. 3). The goodness of fit (R^2) by the Hertzian model was between 0.9403 and 0.9936, with an average goodness of fit of 0.9637 ± 0.018. This increase plateaued between 10% and 12.5%, and no significant difference was found with 10% and 12.5% for both non-sterilised and sterilised hydrogels ($p > 0.05$). Significant higher elastic modulus values were found in sterilised PEG hydrogels compared to non-sterilised hydrogels ($p < 0.001$).

4.2. Surface wettability prior to wear tests

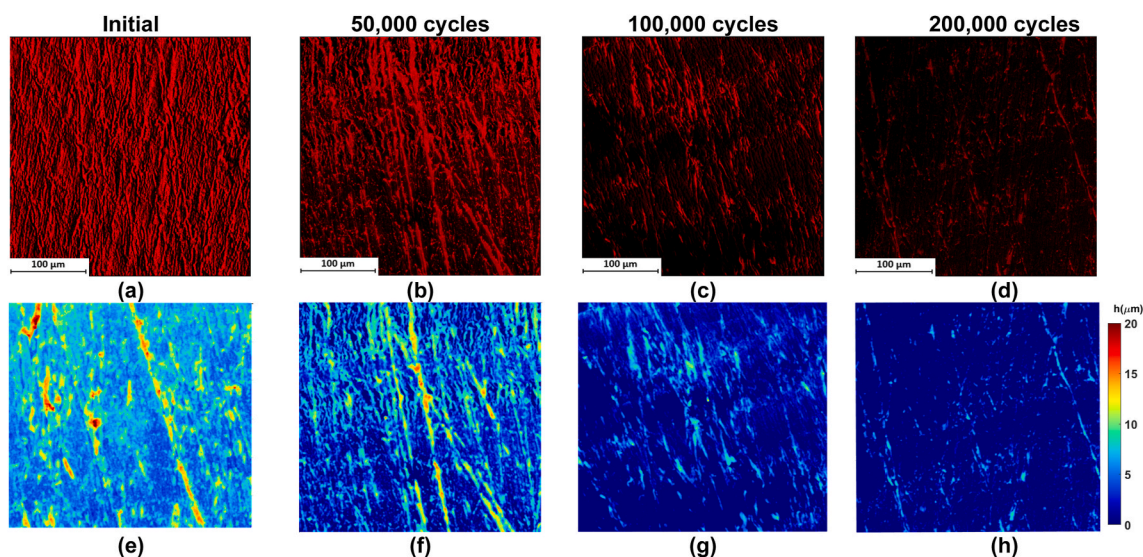The surface wettability of the uncoated, silanisation treated and

Fig. 6. The confocal images (a, b, c, d) and hydrogel thickness maps (e, f, g, h) of the 10% hydrogel coating during wear test indicating the evolution of hydrogel quantities on XLPE pin surface. (a), (e) before the wear test; (b), (f) after 50,000 cycles; (c), (g) after 100,000 cycles; (d), (h) after 150,000 cycles.
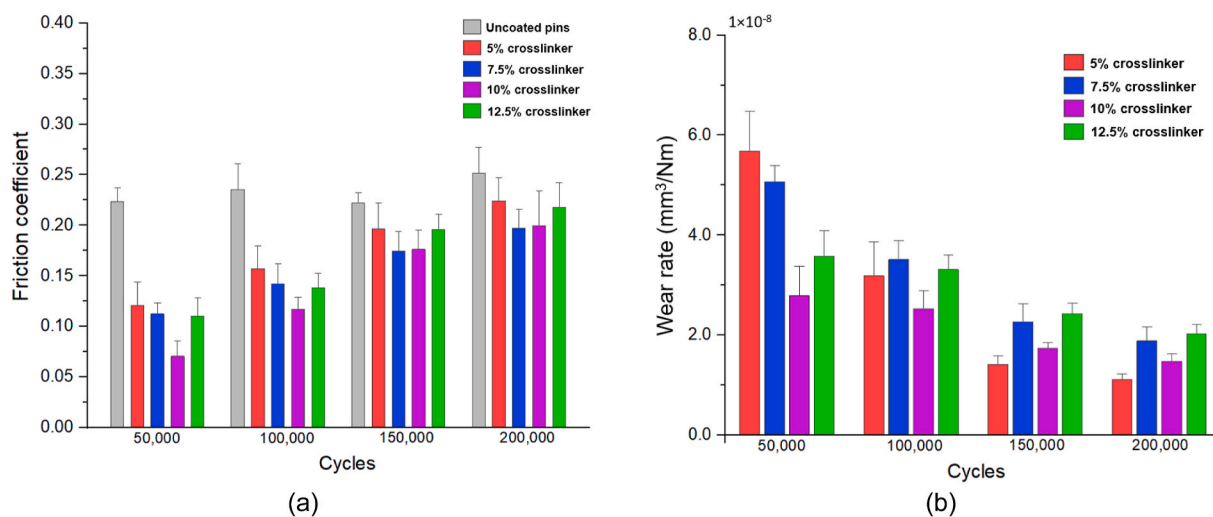

Fig. 7. Comparison of the friction coefficient and wear rates evolution of uncoated and hydrogel coated bearing surfaces during 200,000 cycles of wear tests, and the error bars show one standard deviation from eight repeated tests (a) friction coefficient (b) wear rate.

hydrogel coated surfaces prior to wear testing are shown in Fig. 4. The uncoated XLPE substrate surface exhibited the highest contact angle, with a value of 125°, a typical value for a hydrophobic surface. The silanisation treatment significantly reduced the contact angle to a value of 57° ($p < 0.001$). Further reductions in the contact angle were observed for the PEG hydrogel coated surfaces ($p < 0.001$, on average 47°, 44°, 43°, 47° as crosslinker concentration increased), indicative of hydrophilic surfaces (Fig. 4).

4.3. Friction behaviour of the hydrogel coatings

Although not clear in Fig. 5, the initial high coefficient of friction (CoF) of the coated samples rapidly decreased to low levels (0.05–0.1) over a running-in period of 2000–3000 cycles. This was followed by slow but steady increase in friction over the course of the test reaching a value of ~0.2 at 200,000 cycles. For the first 100,000 cycles, the 10% crosslinker exhibited lowest CoF values (0.06–0.10) with the other hydrogel coatings slightly higher (0.08–0.15), and the 5% crosslinker coating produced higher CoF values (0.10–0.15). In contrast, the CoF of

the uncoated specimens was consistent (0.2–0.25) for most of the test, with a steady increase evident over the last 50,000 cycles. The CoF of all the coatings increased continuously and approached that of the uncoated sample after 200,000 cycles.

Fig. 6 shows a series of confocal images of the 10% hydrogel coating on the XLPE pins recorded at different test durations. The number of pixels above the Otsu threshold in the confocal images (Fig. 6 a-d) was significantly reduced, indicating a reduction in the hydrogel coating thickness and coverage (Fig. 6 e-h) as the testing progressed.

The CoF values and wear volume rates have been summarised in Fig. 7a and b, with the averages for each 50,000 cycles. As the tests progressed the CoF appears to increase, while the wear rate decreases. For a better comparison between the friction and wear, the average wear rate was plotted against the average CoF value of each hydrogel coatings for every 50,000 cycles in Fig. 8. For the first 100,000 cycles, the 10% coating exhibited the lowest friction and wear, while the 5% and 7.5% showed higher friction and wear. However, no obvious correlation was observed between the friction/wear performance and crosslinking for the 150,000 and 200,000 cycles time points.
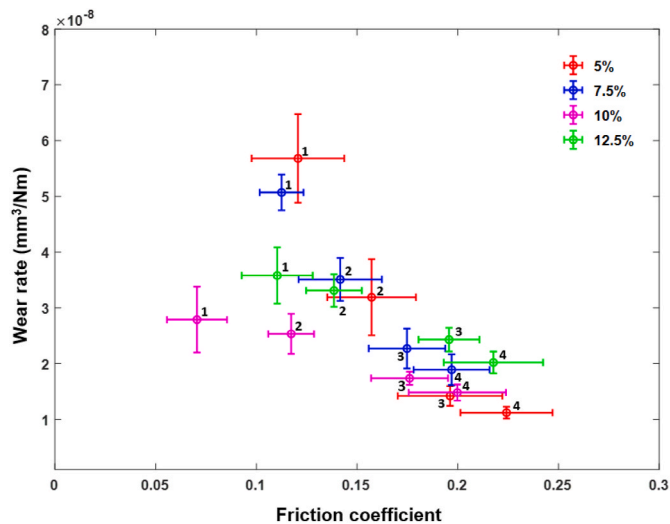
Fig. 8. The wear rate as a function of CoF for all the hydrogel coatings and each 50,000 cycles (1 denotes 50,000 cycles; 2 denotes 100,000 cycles; 3 denotes 150,000 cycles and 4 denotes 200,000 cycles); the error bars show one standard deviation from eight repeated tests.

The hydrogel coating coverage and the average coating thickness obtained from the confocal measurements are shown in Fig. 9. Prior to the wear testing, the coverage of the PEG coatings was close to 100% (denoted by 1 in the plots) for all the coatings tested, and no significant difference was found between the 7.5%, 10% and 12.5% crosslinker concentrations ($p > 0.05$), while at 5% a lower coverage (~98%) was observed. The average thickness values ranged between 4 and 8 μm, with an increase of the crosslinker concentration resulting in an increase in thickness. As the tests progress, the coating coverage decreases, while the coating thickness reducing during the first 100,000 cycles before plateauing (see Fig. 9).

The histograms of coating thickness (see Fig. 10) indicate the thickness evolved from a near normal distribution before tests towards to a right-skewed distribution with test duration. The thickness distributions of the 10% and 12.5% coatings were less skewed than those of the 5% and 7.5% at 100,000 cycles.

The CoF and wear rate values as a function of coating coverage replotted from Figs. 7 and 9 are summarised in Fig. 11. The CoF decreased while the wear rate increased with the increased coverage. As

the crosslinker concentration increased from 5% to 10%, the coating with higher crosslinking exhibited a higher CoF but lower wear rate at each coverage. The data was fitted to a fractional coverage model [36] ($R^2 = 0.71$), with a fitting equation of CoF $= \mu_0 + \theta \times (0.028 - \mu_0)$ shown as a dashed line in Fig. 11a. For reference, a dotted line representing the average CoF of uncoated pins ($\mu_0 = 0.22$), which was determined for the first 100,000 cycles, was added to the plot (denoted as uncoated in Fig. 11a). The CoF data of the 12.5% was significantly higher than those of the other coatings and deviated from the fitting curve ($p < 0.001$). The wear rate of the 12.5% was significantly lower than those of the 5% and 7.5%, but higher than that of the 10% ($p < 0.001$).

4.4. Substrate surface roughness

The initial surface roughness values (Ra, Rq, Rsk) of the hydrogel coated surfaces were lower than the uncoated XLPE substrate surfaces with smaller standard deviations (Table 1), this is likely due to the micro valleys of the rough surfaces being filled with hydrogel. Prior to wear testing, no significant differences were found in the Ra and Rq values of the coated samples ($p > 0.05$), although the 12.5% crosslinker coating had a higher standard deviation compared to the other coating surfaces (Fig. 12).

By end of the wear tests, the Ra and Rq values reduced for both uncoated and coated surfaces, although the reduction for the uncoated surfaces was significantly lower ($p < 0.001$) (in Fig. 12 a, b). In addition, the roughness profiles had more negatively skewed distributions (Rsk<0) after testing, with the exception of the 10% coating (Fig. 12c). The Rsk value of the uncoated XLPE surface went from positive large skew to large negative, 0.71 to −0.6 ($p < 0.001$). The post-test Ra and Rq values were higher with increasing crosslinker concentrations for 5%, 7.5% and 10% crosslinker hydrogel coatings, with significant differences found ($p < 0.05$). The 12.5% coating had similar values of Ra and Rq but with higher standard deviations, compared to the 10% coating.

5. Discussion

This study showed the increase of elastic moduli observed with increasing crosslinker concentration for sterilised and unsterilised PEG hydrogels (Fig. 2). The gamma irradiation almost doubled the elastic modulus values at each crosslinker concentration. Previous studies have shown that the mechanical properties of soft hydrogels can be tailored by controlling the degree of crosslinking, via crosslinker concentration [12], crosslinking route [37], or deposition temperature [19]. The
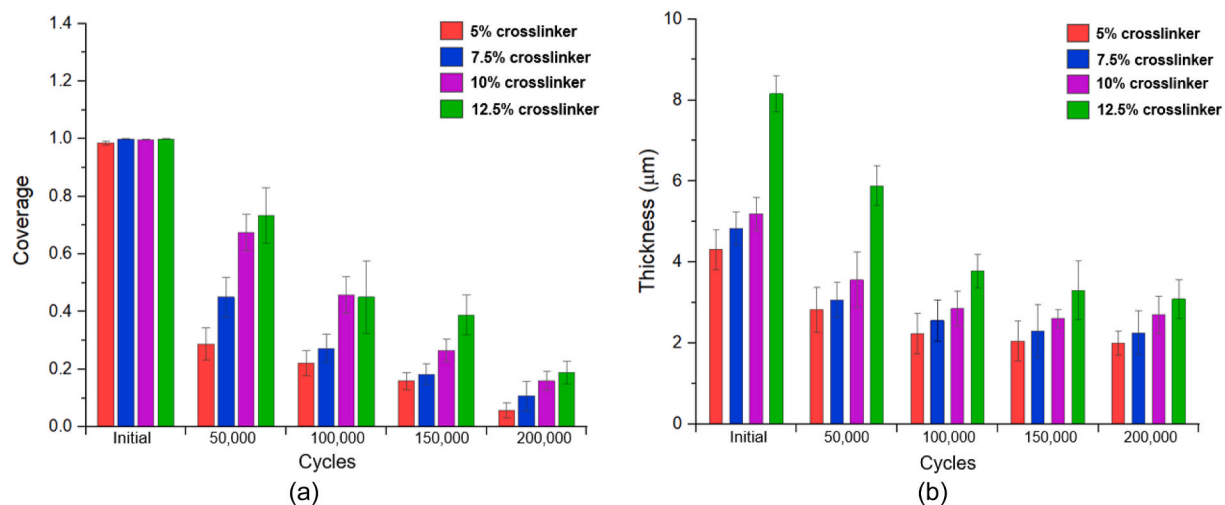

Fig. 9. Hydrogel coating coverage and average thickness evolution for the first 200,000 wear cycles: (a) hydrogel coating coverage, with the error bars showing one standard deviation of the data obtained from the 32 confocal images for each coating at every 50,000 cycles (b) average thickness, with the error bars showing one standard deviation of the data obtained from 32 confocal images with 512 × 512 pixel sites counted for each image.
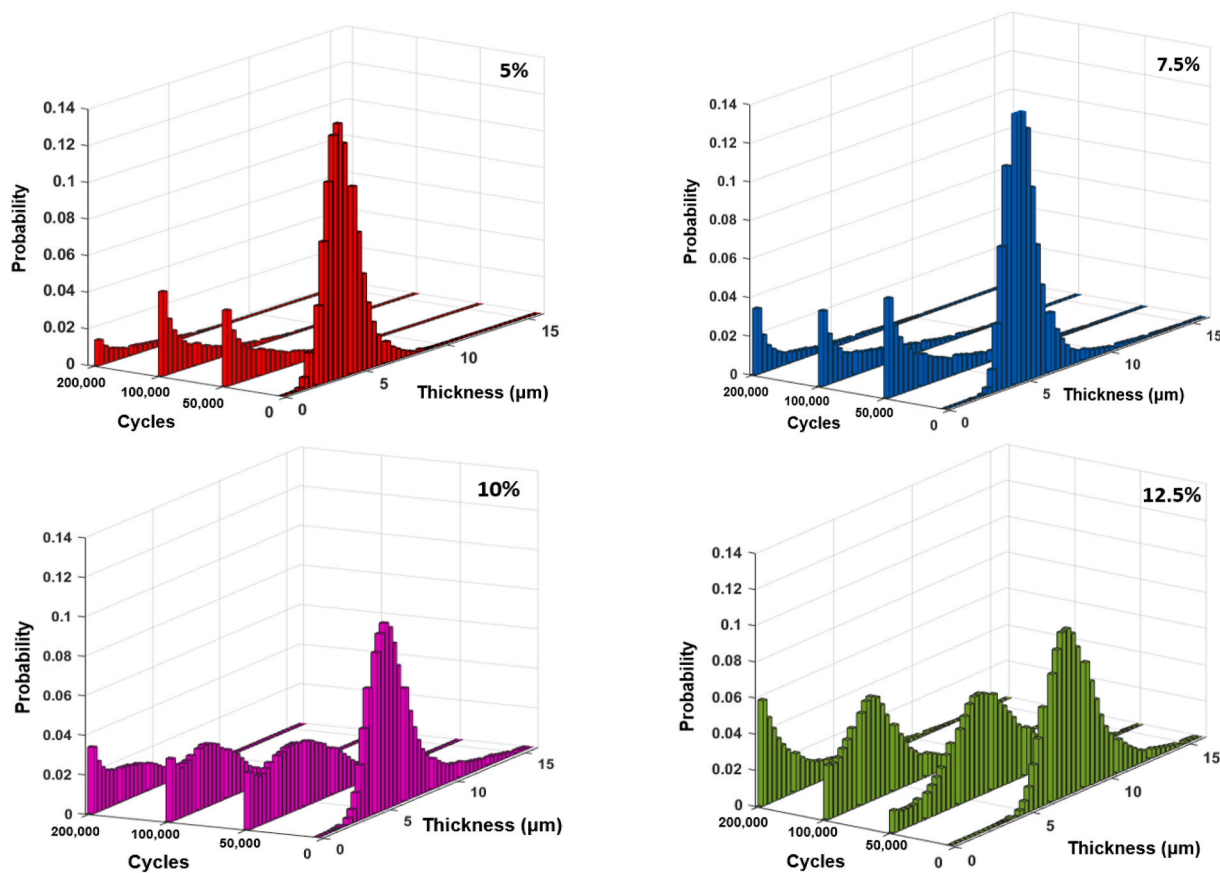
Fig. 10. Exemplar histograms of hydrogel coating thickness distributions for each hydrogel coating with bin width of 0.34 μm from data acquired from 291 μm × 291 μm scanning area with total data points of 512 × 512.
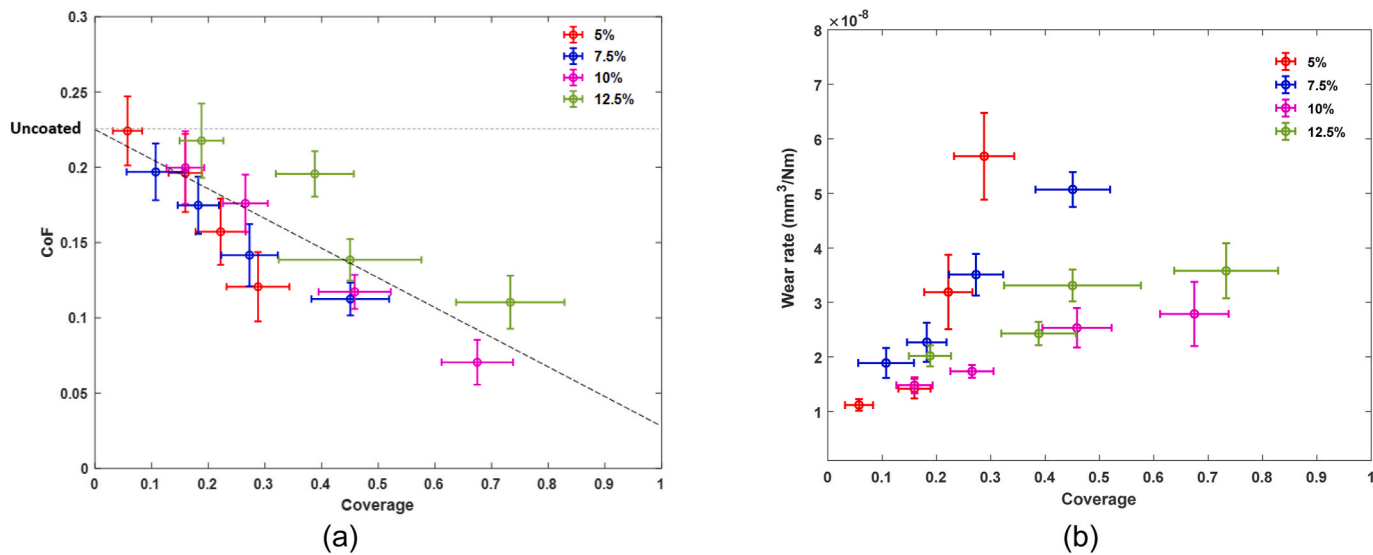

(a)

(b)

Fig. 11. The CoF and wear rate values as a function of coating coverage during 200,000 cycles of wear tests.

Table 1
Initial roughness measurements for XLPE substrate and hydrogel coating surfaces.

	Ra (μm)	Rq (μm)	Rsk
XLPE substrate surface	0.85 ± 0.10	1.12 ± 0.14	0.71 ± 0.08
Hydrogel coating surface	0.54 ± 0.06	0.69 ± 0.07	-0.12 ± 0.31

mechanical properties of hydrogels have been linked to the mesh size in literature [7]. A significant difference in the swelling ratios were observed for the sterilised and unsterilised PEG hydrogels in a previous study [38]. The gamma irradiation can increase crosslinking by producing free radicals which will react with target molecules to form polymer chains or network, reducing the mesh size and resulting in an increased elastic modulus and decreased swelling ratio.
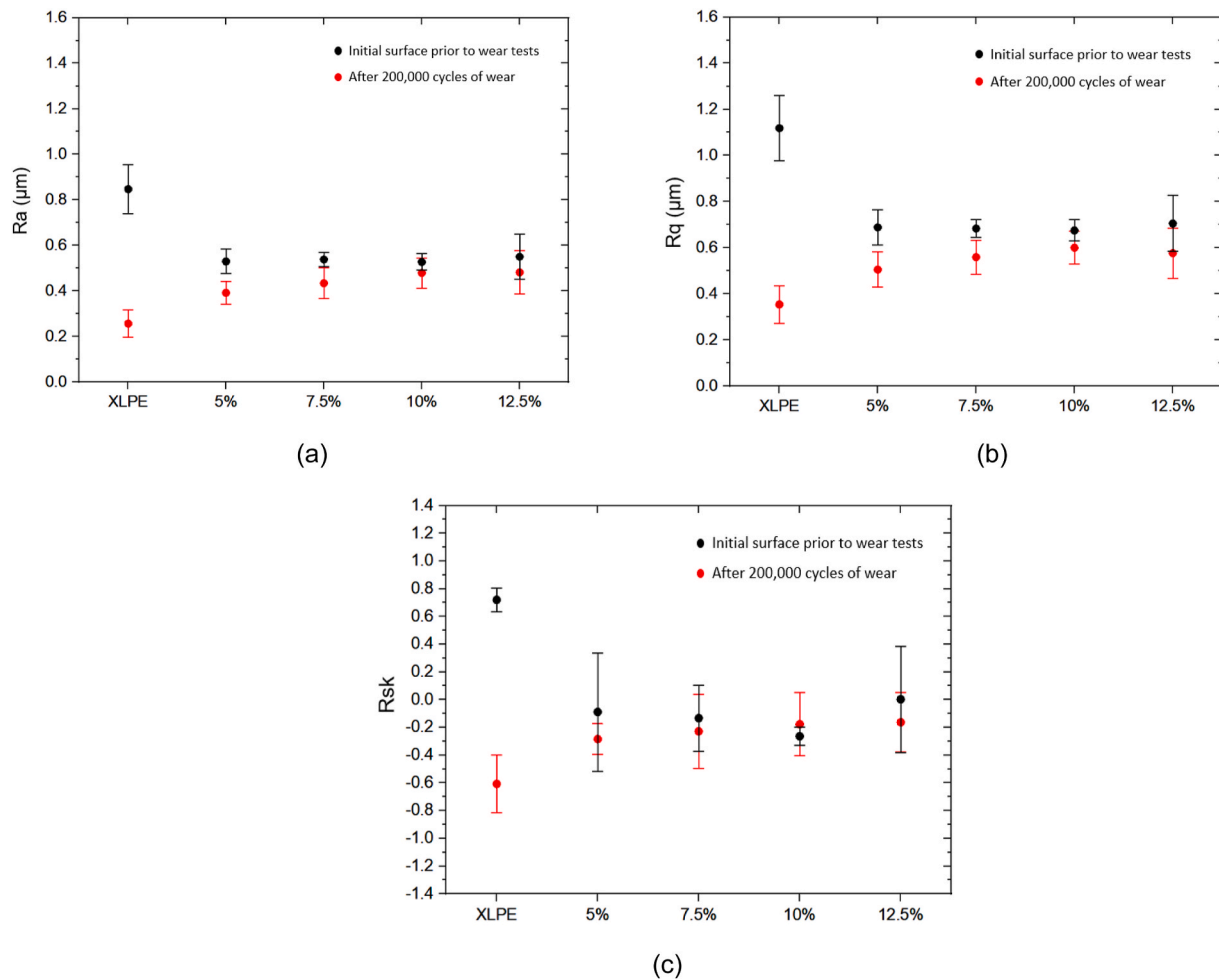
Fig. 12. Surface roughness change prior to and by end of 200,000 cycles of wear tests: (a) Ra; (b) Rq; (c) R*sk*.

While the indentation measurements of the bulk properties of the hydrogels will likely not fully represent the properties of the much thinner coatings, which are extremely difficult if not impossible to measure directly, it is believed the relative variations (i.e. the effects of crosslinking and gamma sterilisation on the elastic moduli) will be indicative of both hydrogel systems. It is challenging to measure the elastic moduli of thin hydrogel coatings, as the measurements can be significantly influenced by the underlying stiffer substrate and the flow confinement for the hydrogel in the micro-valleys of substrate surface.

The hydrogel coatings significantly improved the wettability of the surfaces, imparting superior lubricity and lower friction coefficients (Figs. 4 and 5). This is in agreement with the study by Seo et al. [39], where the surface wettability was not influenced by the degree of crosslinking.

The evolution of the hydrogel coatings was correlated with the CoF values (Figs. 5 and 6). The confocal imaging indicated that the hydrogel coating filled the micro valleys of the substrate surface, see Fig. 6. As the wear test progresses, the nature of the contact changes as the gel on top of the substrate asperities is removed, changing from a pure hydrogel (against CoCr) contact to a combined XLPE substrate/hydrogel against CoCr contact. The friction behaviour of the hydrogel coating can be related to the interstitial fluid response resulting from the compression of the fluid filled hydrogel and the formation of a fluid film between the gel and solid contacts [26,40]. Therefore, the interstitial fluid load support decreases with a reduced coverage of hydrogel coatings, resulting in an increased hybrid XLPE/gel vs CoCr contact and thus, an increased CoF (Fig. 11a).

The wear volume rates of hydrogel coatings were also obtained from

quantitative analyses of confocal microscopy (Fig. 7b). The wear rates characterised by the confocal method are not affected by dehydration of hydrogel coating or the wear of the underlying XLPE substrate. Lower crosslinker concentrations tended to have higher wear rates (Fig. 11b). It is hypothesised that the mechanical strength of the hydrogel coating is increased by crosslinking, which leads to a reduction in the wear rate.

The lower crosslinked coating tended to have lower CoF values compared to higher crosslinked coating with the same coating coverage (in Fig. 11a), however, the low friction could not be maintained due to high wear rates exhibited by low crosslinked coatings (in Fig. 11b). The increased crosslinking is likely to increase the stiffness of the hydrogel coatings and reduce the amount of fluid lubricant in the hydrogel coating. Both effects result in higher friction. Similar trends of CoF value increasing with the degree of crosslinking were found in previous studies [27–29], with the CoF of 12.5% crosslinker coating exhibited signifi-cantly higher CoF despite forming a thicker coating (Figs. 9b and 11a). Overall, the 10% coating exhibited the lowest friction and wear during the first 100,000 cycles (in Fig. 8). The lower wear rate of the 10% coating resulted in higher coverage, which reduced hybrid XLPE/gel vs CoCr contact and produced a lower CoF. No obvious trend was observed for all the coatings from 150,000 to 200,000 cycles as the friction and wear behaviours were mainly governed by the hybrid XLPE/gel vs CoCr contact due to low hydrogel coating coverage.

The CoF was stable for the uncoated bearing couples for the first 150,000 cycles of testing, then a continuous increase in the CoF was observed for the last 50,000 cycles (Fig. 5). This is likely due to plastic deformation of the XLPE surface resulting in an increase in the real contact area and consequently greater adhesion force in the contact, as

observed by Niemczyk et al. [41]. The roughness profiles of the uncoated surface before and after wear testing in Fig. 9 also suggest that the asperities are either removed or undergo plastic deformation during wear. In contrast, the CoF values of the hydrogel coatings increased at a steady rate until 150,000 cycles before plateauing (Fig. 5).

At some point during the tests, it appears that the valleys in XLPE substrates helps prevent further hydrogel removal, which results in a decreased wear rate as tests progressed, but increased friction. The 'hybrid' XLPE/gel vs CoCr contact seems to stabilise after 150,000 cycles (see Fig. 5). This hybrid contact appears to reduce solid-solid interactions, possibly due to the interstitial fluid support offered by the hydrogel, which reduces the wear rate, as evidenced by the higher final values of Ra, Rq, and Rsk compared to the uncoated pins (see Fig. 12). In addition, the higher crosslinked gels appear to protect the asperities from being removed for longer, resulting lower wear rates (see Figs. 7b and 12) and this appears to be linked with the increases mechanical strength of the hydrogel coating with high crosslinking.

6. Conclusion

This study has investigated the effect of crosslinking on the mechanical and tribological properties of PEG-based hydrogel coatings on XLPE substrate. Nanoindentation tests demonstrated that the elastic moduli for the PEG hydrogels increased with crosslinker concentration and significantly increased by gamma sterilisation treatment.

The evolution in hydrogel coating of thickness, coverage and wear rates were characterised by the confocal microscopy at every 50,00 cycles of wear tests. The PEG-based hydrogel coatings lowered the friction compared to uncoated pins, although the friction gradually increased during 200,000 cycles, due to the continuous reduction in coverage of the hydrogel coatings and the increased XLPE vs CoCr contact area. The 10% crosslinked coating exhibited lower friction and wear rate for the first 100,000 cycles compared to the other coatings investigated. No obvious correlation was found between crosslinking and the friction and wear performance at the 150,000 and 200,000 cycles timepoints due to the low coating coverage. The hydrogel coatings in the micro-valleys of the substrate surface protect asperities from being removed at hybrid XLPE/gel vs CoCr contact, compared to a bare XLPE vs CoCr interface, helping to maintain lower CoF, with increased crosslinking retaining this behaviour longer.

Authorship contribution statement

Dichu Xu: Conceptualization, Methodology, Investigation, Visualization, Writing - Original Draft, Writing – review & editing. Terry Harvey: Methodology, Resources, Writing – review & editing. Janire Martínez: Resources. Eider Begiristain: Resources. Cristina Domínguez-Trujillo: Resources, Writing - Original Draft. Laura Sánchez-Abella: Resources, Writing – review & editing. Martin Browne and Richard B. Cook: Project administration, Funding acquisition, Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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