Acta Biomaterialia 6 (2010) 4698–4707

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Wear rate evaluation of a novel polycarbonate-urethane cushion form bearing for artificial hip joints

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ARTICLE INFO

Article history:
Received 21 April 2010
Received in revised form 8 July 2010
Accepted 9 July 2010
Available online 13 July 2010

Keywords:
Total hip replacement
Bio-ferrography
Filtration
Polyurethane
Fatigue

ABSTRACT

There is growing interest in the use of compliant materials as an alternative to hard bearing materials such as polyethylene, metal and ceramics in artificial joints. Cushion form bearings based on polycarbonate-urethane (PCU) mimic the natural synovial joint more closely by promoting fluid-film lubrication. In the current study, we used a physiological simulator to evaluate the wear characteristics of a compliant PCU acetabular buffer, coupled against a cobalt–chrome femoral head. The wear rate was evaluated over 8 million cycles gravimetrically, as well as by wear particle isolation using filtration and bio-ferrography (BF). The gravimetric and BF methods showed a wear rate of 9.9–12.5 mg per million cycles, whereas filtration resulted in a lower wear rate of 5.8 mg per million cycles. Bio-ferrography was proven to be an effective method for the determination of wear characteristics of the PCU acetabular buffer. Specifically, it was found to be more sensitive towards the detection of wear particles compared to the conventional filtration method, and less prone to environmental fluctuations than the gravimetric method. PCU demonstrated a low particle generation rate ($1–5 \times 10^6$ particles per million cycles), with the majority (96.6%) of wear particle mass lying above the biologically active range, 0.2–10 μm. Thus, PCU offers a substantial advantage over traditional bearing materials, not only in its low wear rate, but also in its osteolytic potential.

1. Introduction

The natural synovial joint provides low wear over decades, which may be ascribed to the maintenance of a fluid-film that considerably reduces friction by separating the articulating surfaces [1]. The development of a fluid-film is predominantly due to a combination of elasto-hydrodynamic lubrication (EHL) and micro-elasto-hydrodynamic lubrication (μEHL) [2]. EHL is produced when the pressure developed in a converging film of lubricant between two articulating surfaces (e.g. cartilage) is sufficient to cause local elastic deformation of either of the surfaces, keeping them apart [3]. μEHL is a localized form of EHL, whereby pressure perturbations cause substantial flattening of asperities at the material's surfaces, increasing conformity and assisting in the maintenance of a lubricious film [3]. Illnesses such as osteoarthritis or traumatic injury might affect the tribology, to the extent that the natural joint bearing system is totally destroyed, causing pain and disability.

Total hip joint replacement (THR), the common treatment in such cases, was revolutionized half a century ago by Sir John Charnley, who introduced a system consisting of a stainless steel femoral stem head combined with an ultrahigh molecular weight polyethylene (UHMWPE) acetabular cup. This metal-on-polyethylene (MoPE) system is the gold standard treatment, which presently demonstrates a survival rate of 79% after 11 years and 51–60% after 25 years, in young patients (<55 years) [4]. Failure of this implant is mostly due to aseptic loosening [5,6]. Aseptic loosening is associated with osteolysis and bone resorption, induced by wear particles generated from the implant [7,8]. The MoPE artificial joint operates in a mixed-mode lubrication regime, in which the bearing surfaces are not completely separated and the load is carried partly by the fluid pressure and partly by the contacting asperities [9]. Abrasive and/or adhesive wear mechanisms can thus lead to particle generation. Traditional MoPE systems have been reported to have a wear rate of 30–100 mm^3 per year [10]. Other hard-on-hard bearings such as metal on metal (MoM) and ceramic on ceramic (CoC) produce lower wear rates than the conventional MoPE joint due to their hardness. The short-term clinical performance of MoM and CoC is reported to be 0.3 and 0.01–0.1 mm^3 per million cycles (Mc) (the equivalent of one year), respectively [10]. Although a low wear

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doi:10.1016/j.actbio.2010.07.011

volume is an important factor governing the long-term clinical outcome of THR, other factors such as particle size, morphology, material chemistry and biological response to the wear particles must also be taken into account. MoM prostheses, for example, have not been associated with osteolysis and demonstrate a low wear volume; however, wear particles generated by MoM prostheses are significantly smaller than UHMWPE particles produced by MoPE prostheses. As a result, a higher number of metal particles is produced overall (6.7×10^{12}–2.5×10^{14} metal particles per year, compared to 5×10^{11} UHMWPE particles per year produced by a conventional MoPE prosthesis) [11]. Nanometer-sized metal particles have been shown to be disseminated throughout the body – in the lymph nodes, spleen and bone marrow [12,13]. The high activity of metallic nano-debris results in enhanced corrosion and release of metal ions to the joint. Certain metal ions have been shown to induce hypersensitivity and implant intolerance reactions [14,15].

The use of compliant layer joints in artificial joints to promote EHL and μEHL and to reproduce the tribological function of the joint has gained much interest in recent years. Unlike rigid materials, employing a compliant hydrophilic polymer layer in the acetabular cup could restore the natural lubrication regime of the natural joint (full fluid-film lubrication), to further reduce wear. Polycarbonate-urethane (PCU), for example, has shown promising results as a candidate material for hip arthroplasty in terms of its mechanical properties, frictional behavior and lubrication, which are similar to natural cartilage [2,16–18]. However, there is paucity on the report of wear of a final implant configuration composed of this material. The introduction of new bearing materials should be supported by accurate descriptions of the number, size distribution and volume of wear particles generated, for instance, via in vitro simulation. Many simulators in use to evaluate wear apply a single cycle force along one axis, while motion is produced by the movement of the cup around this axis. In contrast, hip motion is produced in vivo by complex movements of the femoral head around an axis through the acetabular cup. Since wear patterns and rates depend on the nature of loads and motions applied to the hip joint, it is important to simulate correctly the anatomical positioning, movement and physiological loads that occur during normal gait, even if choosing to ignore the wider ranges of load and motion that are applied during various activities.

The evaluation of wear from such simulations is typically done by filtration of wear particles from the lubricant (serum) or by measurement of gravimetric changes in the implant's weight. In the current study, we employ both methods as well as a novel bio-ferrography method, which, to the best of our knowledge, has not been applied before for isolation of PCU particles. Ferrography is a method of particles separation onto a glass slide based upon the interaction between an external magnetic field and the magnetic moments of the particles suspended in a flow stream. By determining the number, shape, size, texture and composition of particles on the ferrogram, the origin, mechanism and level of wear can be determined [19,20]. Bio-ferrography (BF) is a recent modification of the conventional analytical ferrography that was specifically developed to allow for magnetic isolation of target cells or tissues [21–23]. Among the strengths of this method that are relevant to this study one may mention: (1) the ability to count the isolated particles while analyzing their shape and surface morphology microscopically and determining their chemical composition; (2) an extremely high selectivity and sensitivity; (3) the applicability to any liquid sample; and (4) samples as small as 1 μl and target particles as small as several nanometers can be analyzed [24]. So far, BF has been used to separate polyethylene wear debris from hip simulator fluid [25].

The goals of the current study were, therefore, to: (i) provide a comprehensive description of the wear characteristics of PCU as a compliant bearing material, and (ii) validate BF as a legitimate method for the wear evaluation of PCU.

2. Materials and methods

2.1. Implants

Six polycarbonate-urethane (Bionate 80A, DSM-PTG) acetabular components (buffers, Fig. 1a) with a 46/40 outer/inner diameter (mm) were used in the simulation. Each buffer was coupled with a 40 mm CoCr alloy spherical femoral head. Six additional buffers were used as controls: $n = 3$ were maintained at room conditions (25 °C, ~30% humidity) to serve as dry controls, and $n = 3$ were maintained throughout the experiment in the test medium (37 °C) and will thus be referred to as soak controls. All components were supplied for analysis in their sterile packaging (Active Implants Corp. (AIC), Israel).

2.2. Simulator

A specially designed hip simulator (FSM, AIC, R&D Center, Israel) with anatomical positioning was used in this study (Fig. 1a). This hip joint simulator has six articulating stations, each with four independently controlled motions: abduction–adduction, flexion–extension, internal–external rotation, and vertical loading, programmed according to ISO-14242 (Fig. 1b). The simulator was equipped with motion and force control systems capable of generating the angular movements of the femoral component with an accuracy of ±3° at the maxima and minima of the motion, maintaining the magnitude of the maxima and minima of the force cycle to a tolerance of ±3% of the maximum force value, and ±1% of the cycle time.

2.3. The lubricant

We used adult bovine serum, 0.2 μm filtered (Biological Industries, Beit Haemek, Israel), which was diluted (1:4 by volume) with distilled water.

2.4. Reagents

The following reagents were used: (1) hyaluronidase, 400–1000 U mg^{-1} (Sigma, H3506), (2) proteinase K, $\geqslant 30$ U mg^{-1} (Sigma, P6556), (3) trypsin, 1000–2000 BAEE U mg^{-1} (Sigma, T4779), and (4) erbium chloride ($ErCl_3$) (Sigma, 449792).

2.5. Wear simulation

The six samples undergoing simulation were pre-soaked for 48 h in the test medium (1:4 water-diluted bovine serum) before beginning the test. Next, they were cleaned and dried, and their initial weight was recorded for reference. Five of the samples were then randomly assigned to undergo full gait simulation according to ISO-14242. The sixth specimen served as a load-soak control and was only loaded with the vertical load component. The simulation was conducted over the duration of 8 million cycles (Mc), with stops at 0.5 and 1 Mc and successive 1 million cycle intervals. At each stop, the samples were removed from their holder, wiped with lint-free wipes (Kimwipes®, Kimberly-Clark) and dried in open air for 30 min, weighed and inspected visually. Samples of the test medium were taken for wear evaluation, as described below, and the lubricant was completely replaced with fresh medium for further simulator operation.

2.6. Wear analysis

2.6.1. Gravimetric measurements

The wear rate was determined from gravimetric measurements by linear regression of the decrease in the implant weight over

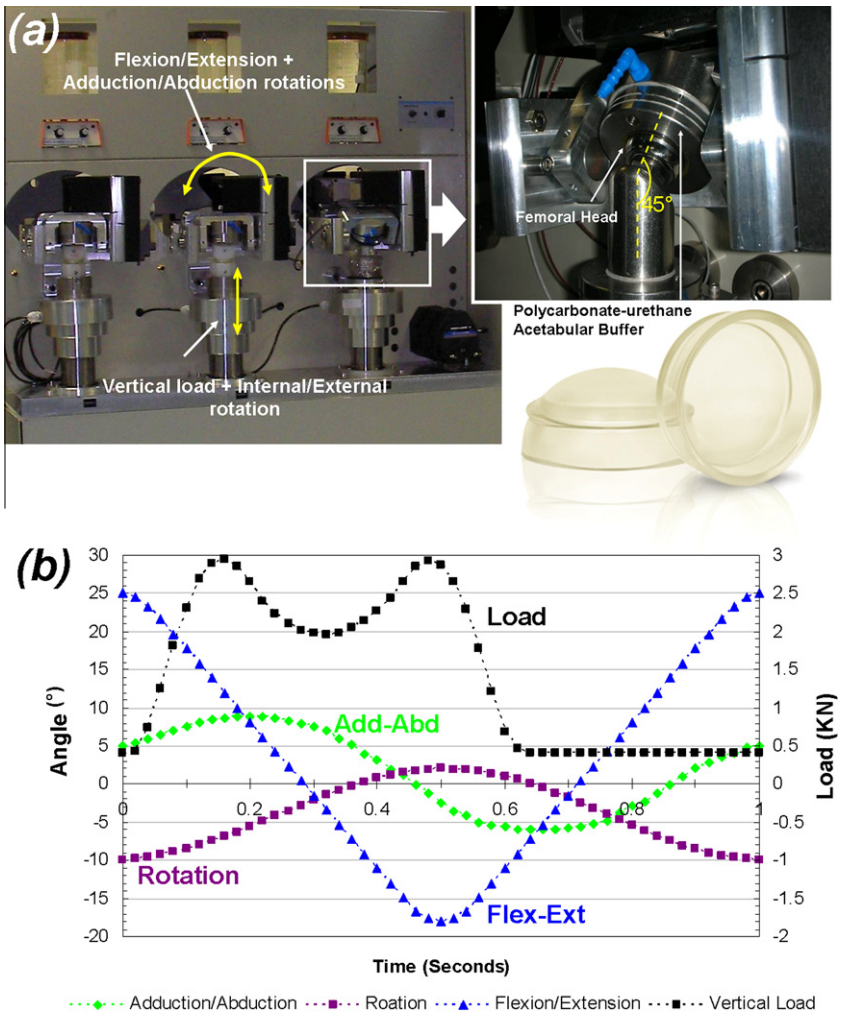

Fig. 1. The physiological anatomical hip joint simulator setup used in the study (a) and load/movement settings representative of a single load cycle, based on ISO-14242 (b).

time. Since PCU is hygroscopic to some extent (1–2% w/w) and may undergo geometrical deformation due to creep, it is necessary to take into account these effects. The adjusted characteristic curve of weight loss was calculated with respect to the soak controls:

$$\text{Wear rate} = \frac{\partial\{\, w(t) \,-\, c(t)\}}{\partial t} \tag{1}$$

where $w(t)$ and $c(t)$ represent the average weight measurements of the test specimen and control soak specimen, respectively, at time point t. The gravimetric measurements were repeated for: (1) a group of identical implants ($n = 3$), which were maintained throughout the experiment in the test medium (37 °C) and will thus be referred to as soak controls, and (2) a load-soak control (specimen #6), which was loaded vertically – similar to the test specimens.

2.6.2. Filtration

2.5 ml samples of the removed test medium were taken for particulate analysis following thorough stirring. Protein particles present in the medium were then digested by 1:1 dilution with an enzymatic cocktail (hyaluronidase, trypsin and proteinase K), originally suggested by Meyer et al. [25], and overnight incubation at 37 °C. The solution was then diluted 10:1 in distilled water. One-hundred microliters of the processed solution were filtered through a 13 mm polycarbonate membrane with 0.08 μm pore size (GE Osmonics), and placed in Pop-top plastic filter holders (Whatman). Upon drying, the filters were placed on aluminum discs, gold-sputtered, and their entire surface area was scanned for wear particles at a 150× magnification by scanning electron microscope (SEM, Jeol JSM-6300) at an accelerating voltage of 5 kV. The wear particles that were identified at 150× were subsequently imaged, one by one, at higher magnification (1000×) and traced by image processing software (SigmaScan Pro), which provided an effective diameter, perimeter, area, and form factor (φ):

$$\varphi = \frac{4\pi \cdot \text{Area}}{\text{perimeter}^2} \tag{2}$$

The form factor is a dimensionless quantity that reflects the deviation of the feature's outline from a circle shape. It ranges from 0 to 1 and is sensitive to variations in perimeter curvature. Based on the calculated effective diameter of each particle (D_n), each particle n was assigned a volume by approximating it to a sphere. The volume was then transformed to weight by multiplying by the material density ($\rho = 1.19\ \text{g cm}^{-3}$) so that the weight sum of wear particles in the sample is depicted by:

$$w(t) = \rho \cdot \sum_n \frac{\pi (D_n)^3}{6} \tag{3}$$

Finally, for the tested 100 μl, which represents 1:3000 of the original volume of test fluid, a correction of 3000× was applied to the weight. This process was repeated per sample and per the aforementioned time points. The cumulative wear particle generation was then plotted versus time (in terms of Mc), and the wear rate was calculated as:

$$\text{Wear rate} = \frac{\partial w(t)}{\partial t} \tag{4}$$

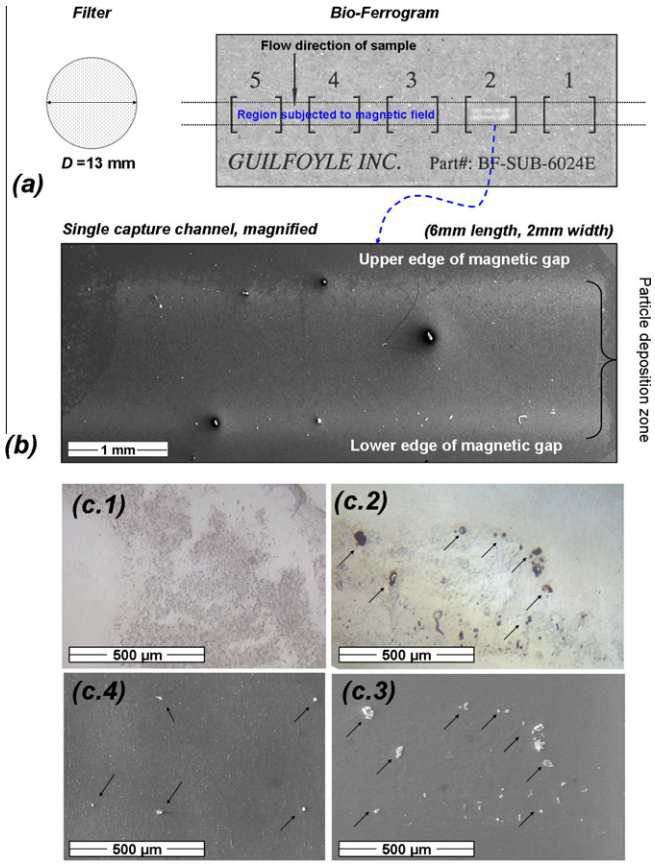

Fig. 2. (a) Schematic view of the area of deposition on the polycarbonate filter, and a macroscopic view of a bio-ferrogram following magnetic capturing of wear particles from five test specimens, each in an individual channel (1–5). (b) Magnified (SEM) observation of a capture band demonstrates the intensity of particle capturing close to the edges of the magnetic gap. (c.1) Light microscope image of a bio-ferrogram of a sample of pristine serum, without enzymatic digestion. (c.2) Light microscope image of a bio-ferrogram of a sample of ground PCU in serum, without enzymatic digestion. (c.3) SEM image corresponding to c.2. (c.4) SEM image of a filtration membrane with a sample of ground PCU in serum, without enzymatic digestion.

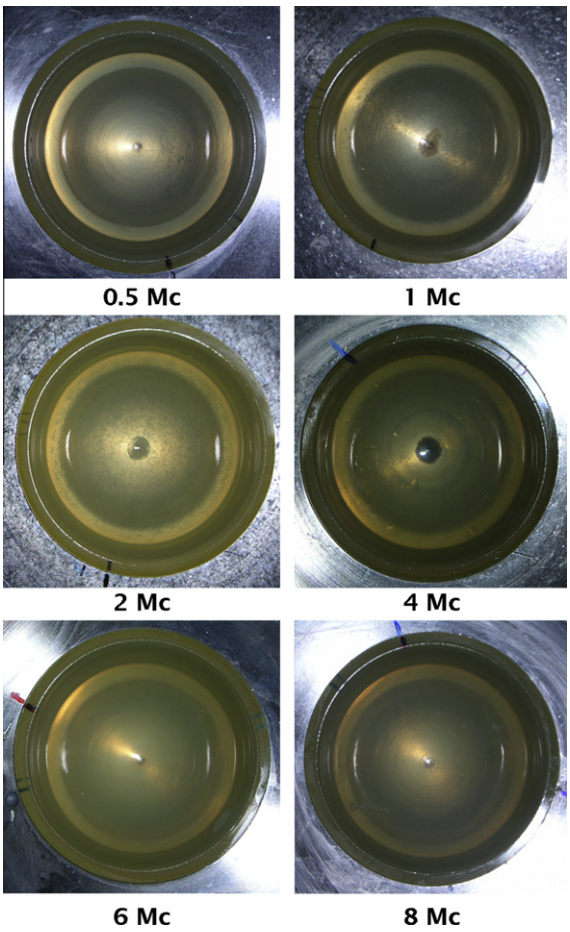

Fig. 3. Photographs of the pliable polycarbonate-urethane acetabular buffer, demonstrating its appearance after 0.5, 1, 2, 4, 6, 8 million load cycles.

2.6.3. Bio-ferrography (BF)

Samples taken from the same stock used for the filtration particulate analysis were treated exactly as described above for protein digestion and 10:1 dilution. One-hundred microliters of the processed solution were taken for BF tests. Magnetization does not naturally occur in synthetic polymers and biological matter; hence, wear particles of such origins must be magnetized prior to BF. In this study, a non-specific magnetization method was used, namely adsorption of the paramagnetic lanthanide cation Er^{3+} [26,27]. A solution of erbium chloride ($ErCl_3$, 10 mM) was prepared and added to the test solution (4:1 by volume). The mixture was then vortexed for 2 min and left to rest for 30 min. A second vortexing was done 1 min before the BF experiment started. A bio-ferrograph 2100 (Guilfoyle Inc.) bench top laboratory instrument, which utilizes a magnetic field across an interpolar gap, was used to collect magnetically susceptible particles. The maximum magnetic field across the gap is 1.8 T; however, the gradient of the field is at a maximum at the edges of the gap, thereby concentrating the deposition at the gap edges as a rectangular band (see Fig. 2a and b). Five fluid samples were introduced into individual reservoirs and passed through a chamber over the magnetic gap at a fixed flow rate of 28 µl min^{-1}, which had been found sufficiently slow to assure full recovery of particles. The particles held in place by the magnetic field were deposited on a glass slide (Fig. 2a), while the remaining fluid flowed out of the chamber. The slides were dried horizontally in a hood, gold-sputtered, and imaged by SEM. The capture band (Fig. 2b) was entirely scanned at a magnification of 150×, and the images (~33) were stitched together to compose the full band. This magnification was chosen as a tradeoff between viewing the broadest field of view and visually identifying individual particles. Processing by image analysis and calculations similar to those described for filtration were used in this case, and the wear rate was calculated from the cumulative particle generation plot, according to Eq. (4).

2.7. Statistics

The results of the isolation method (BF versus filtration) over time was assessed by a repeated-measures analysis of variance (ANOVA-RM), using SPSS ver. 15.0 software. The averaged dependent variables per station ($n = 5$) were the number of isolated particles, diameter, perimeter, area and form factor. These were compared, with the isolation method as the between-group factor while time (Mc) being the within-subject factor. A Tukey post hoc test was used. Data were considered significantly different when $P \leqslant 0.05$.

3. Results

The wear rate of a novel PCU acetabular bearing was evaluated over 8 million simulated gait cycles. Visual inspection of the tested implants showed good results: the articulating surfaces of the PCU

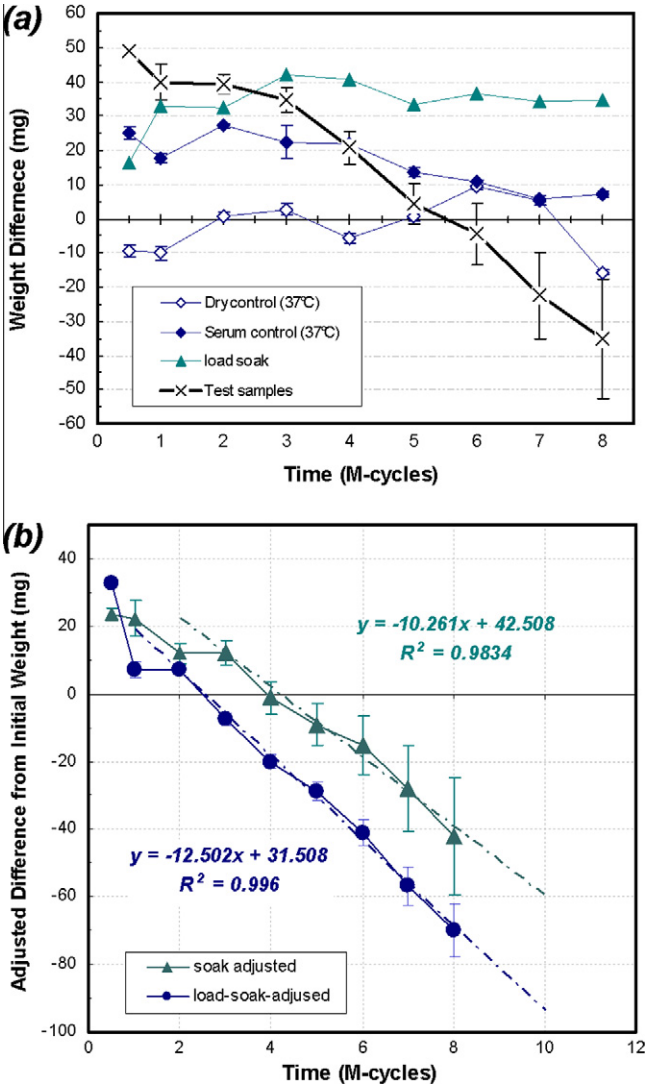

Fig. 4. Gravimetric measurements of the implant and soak controls over the duration of 8 million load cycles (a), and (b) measurements adjusted according to load-soak and soak controls (mean ± standard error of the mean).

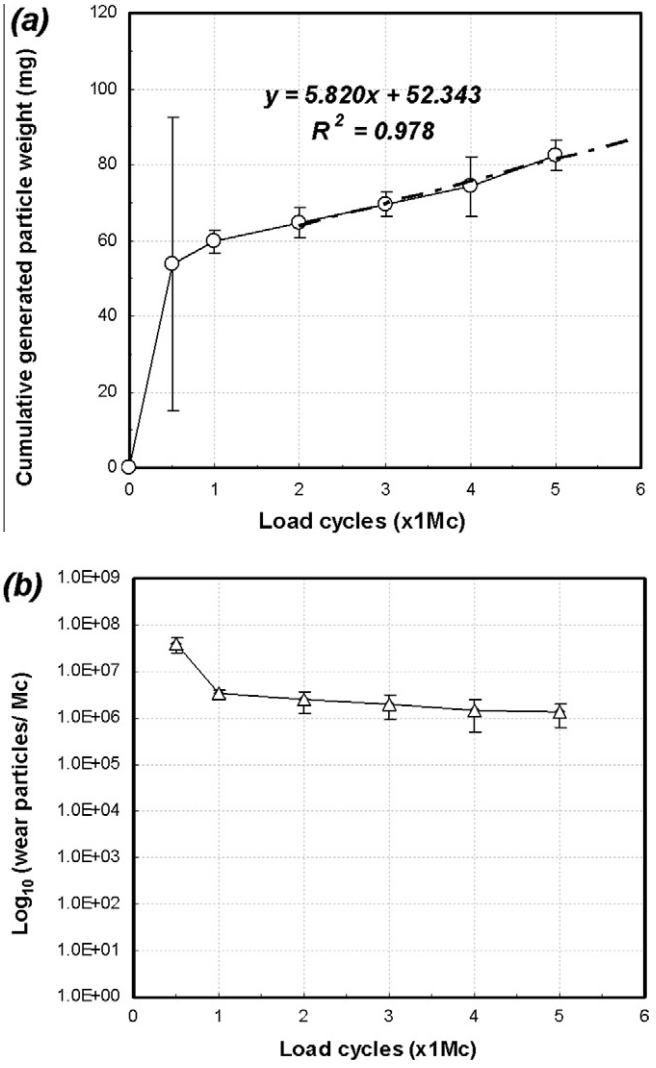

Fig. 5. Cumulative weight of filtration-isolated wear particles (a) and wear particle generation rate during 5 M load cycles (b) (mean ± standard error of the mean).

acetabular buffer remained smooth, and there were no signs of scratches or discoloration (Fig. 3). Wear rate data obtained by the three methods are presented below.

3.1. Gravimetric measurements

Gravimetric measurements of the implants demonstrated an initial increase in weight at 0.5 Mc, followed by a gradual decrease in weight over time (Fig. 4a). The weight of soak controls, placed in the test medium, increased by 14 ± 6 mg on average, whereas the load-soak control increased even more, by 23 ± 13 mg (Fig. 4a). These represent, respectively, an additional 0.12% and 0.2% water absorption compared to the pre-soaked specimens. Taking such changes into account, the implant weights were adjusted at each time point by deducting the differences in the weight of the controls (simple soak or load-soak) from the change in the weight of the tested implants. These results are shown in Fig. 4b. The adjusted weight loss according to the controls was found to stabilize after 2 Mc when the load-soak was considered, or after 3 Mc when the simple soak was considered. Linear approximation of the wear rate in steady-state demonstrated a rate of 10.3 and 12.5 mg Mc^{-1}, respectively, for each adjustment method, with excellent linear fit ($R^2 > 0.98$) (Fig. 4b).

3.2. Filtration

The cumulative amount of wear particles released to the test medium over time was calculated by summing up the weight of particles measured at each time point with those measured at previous time points. The resultant cumulative particle release curve represents the weight of PCU lost over time due to wear (Fig. 5a). The characteristic curve is similar to that described by Clarke et al. [28], with an initial run-in phase of 0.5 M cycles, demonstrating a relatively high wear rate (108 mg Mc^{-1}), followed by a low steady-state wear rate of 5.8 mg Mc^{-1}. The wear rate was calculated based on the results of 2–5 Mc, for consistency with the wear rate evaluated from the gravimetric measurements. When referring to the particle generation rate, it was found that the particle generation rate of 1×10^8 particles Mc^{-1} during the run-in period was decreased to $1–3 \times 10^6$ particles Mc^{-1} after 2 M cycles and remained in this range thereafter (Fig. 5b).

3.3. Bio-ferrography

Several controls were analyzed in this study. These included blank deionized (DI) water with no polymer particles, blank lubricant as in Section 2.3 (see Fig. 2c.1), PCU particles generated

by mechanical grinding of the bulk material and suspended in DI water, and PCU particles generated by mechanical grinding of the bulk material and suspended in the lubricant from Section 2.3 (see light microscope image Fig. 2c.2 and the corresponding SEM image, Fig. 2c.3). In the former two controls, no PCU particles were found on the ferrogram (note the background in Fig. 2c.1 as a result of not using the enzymatic cocktail in this case). In the latter two controls, similar results were found with respect to the size, amount and shape of PCU particles. Fig. 2c.2 and c.3 shows a light microscope image and a SEM image, correspondingly, of the same area on the bio-ferrogram. No enzymatic cocktail was used in the preparation of this sample. Yet, the PCU particles are clearly distinguishable from their precipitated serum background in these figures. Fig. 2c.4 shows a SEM image of the same sample as in Fig. 2c.3, but on a filtration membrane.

Bio-ferrography was found to be very sensitive not only for isolation of PCU wear particles, found in larger numbers than by filtration ($P \ll 0.05$), but also to the presence of other substances in the test medium, e.g. proteins and salts. Sediments were frequently found on the slide (Fig. 2b). Nevertheless, since PCU particles have a different shape from the other materials and a typical rugged structure (Fig. 7), it was possible to distinguish between true wear particles and clatter. Additionally, the energy dispersive spectroscopy (EDS) spectrum of wear particles was similar to that of PCU powder created artificially by grinding the implant material (Fig. 7g). The quantification of generated wear particles by BF was conducted in a similar way to that described for filtration, taking into account measurements in the steady-state phase between 2 and 5 Mc. The wear rate of 9.9 mg Mc^{-1} calculated in this case is in better correlation to the gravimetric measurements than filtration. In comparison to filtration (Fig. 5), BF (Fig. 6) shows a gradual reduction in the wear particle generation rate, from the initial run-in period to steady rate after 2 M cycles. Similar to filtration, the particle generation rate was found to be maximal in the run-in period, 2.3×10^8 particles Mc^{-1}, and then was gradually reduced to 5×10^6–1.5×10^6 particles Mc^{-1} between 2 and 5 Mc. The amount of particles isolated by BF and filtration over time demonstrated significant interaction ($P \ll 0.05$), implying that both parameters converge/intersect at some time.

3.4. Wear particle characterization

Wear particles isolated by filtration and BF were characterized numerically in terms of size and shape (Table 1) over time. Generally, particles were found to have a rugged, non-smooth surface morphology, as demonstrated in Fig. 7 for three representative particle forms: elongated (rod-like) (Fig. 7a and d), globular (Fig. 7b and e) and lamellar (Fig. 7c and f). The surface morphology of these particles was similar to that of ground PCU particles (Fig. 7g). The isolated PCU wear particles were generally of globular shape and had smooth boundaries, as portrayed by average form factor values of 0.75 and 0.83 for particles isolated by filtration and BF, respectively. The effective diameter of particles isolated by both methods was measured, and the distribution of sizes was recorded over time (Fig. 8). The mean particle diameters of isolated particles were found to be 8–13 μm (median: 8–12 μm, range: 1–73 μm) for particles captured by filtration, and 13–18 μm (median: 10–13 μm, range: 3–122 μm) for BF (Table 1). Particles isolated by BF were found to have larger means compared to those isolated by filtration ($P < 0.05$), but the range of sizes generally overlapped (Table 1). A set of ANOVA tests failed to reveal isolation method by time interaction for the geometrical parameters of particles (i.e. differences are not reduced over time).

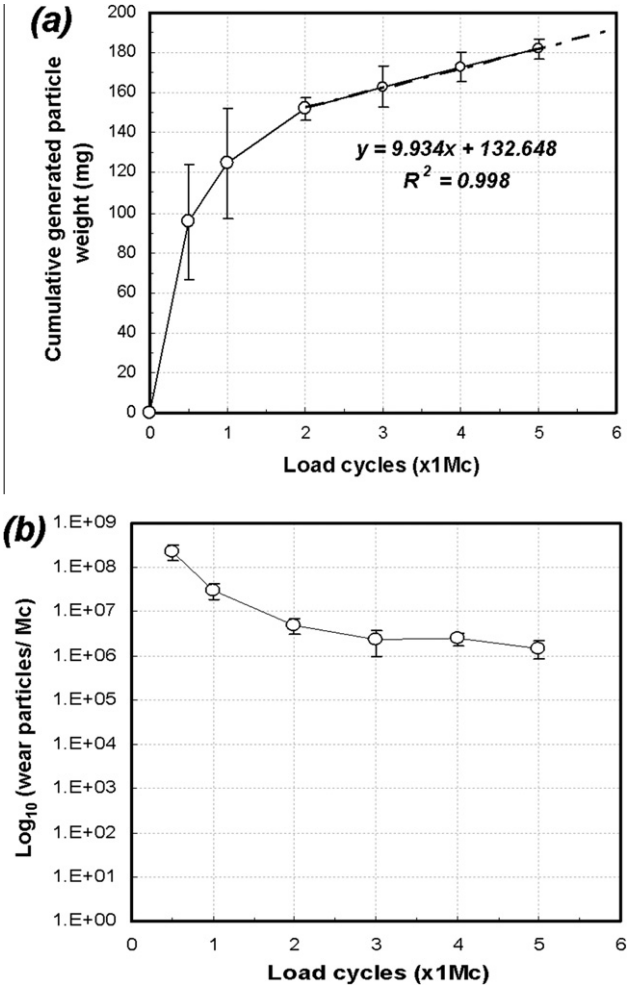

Fig. 6. Cumulative weight of bio-ferrography-isolated wear particles (a) and wear particle generation rate during 5 M load cycles (b) (mean ± standard error of the mean).

4. Discussion

Although artificial joints generally have a long service life, in excess of 15 years, osteolysis and aseptic loosening of the components are significant contributors to a steep decline in the joint survival rate in younger patients in subsequent years [4]. For UHMWPE joints, for instance, the onset of bone resorption and loosening have been associated with a cumulative volumetric wear of 520 ± 80 mm^3 [29]. The investigation of wear patterns may, therefore, hold important information regarding the expected long-term performance of a bearing system with regard to material selection and design.

Previous works have shown the great potential of PCU as a compliant bearing material which can articulate with low frictional torques thanks to its ability to support μEHL [2,9,18]. It remains, however, to be elucidated if a low-modulus cushion bearing designed to help mimic the cushioning and tribological regime of a healthy human hip joint can be durable enough to withstand millions of load cycles. This was done in the current study by simulating a CoCr-on-PCU bearing system for 8 million load cycles.

Bio-ferrography was proven to be an effective method for the determination of wear characteristics of the PCU acetabular buffer. Specifically, it was found to be more sensitive towards the detection of wear particles compared to the conventional filtration method, and less prone to environmental fluctuations than the

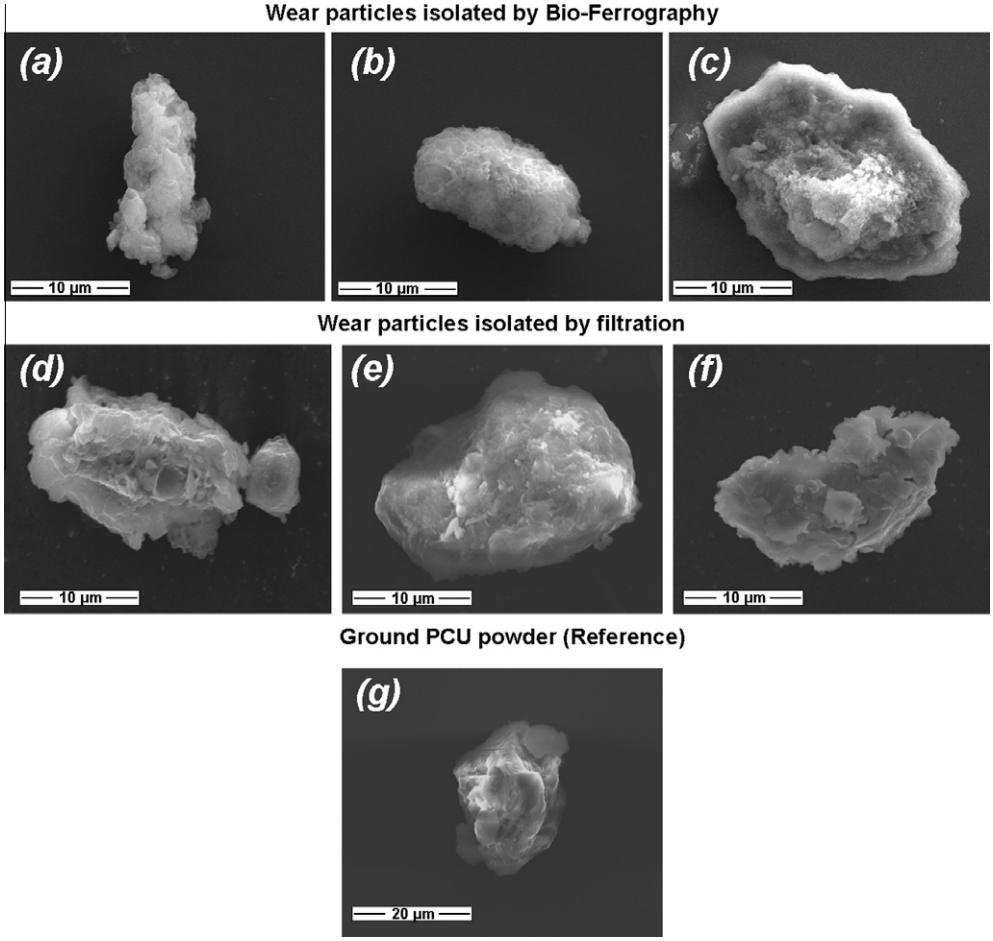

Fig. 7. Representative SEM micrographs of polycarbonate-urethane wear particles isolated by bio-ferrography (a–c) and filtration (d–f). Particles were found to have elongated (a, d), globular (b, e) or lamellar (c, f) shapes. All shapes have surface morphology similar to that of ground PCU powder (g).

gravimetric method. The weight increase due to water absorption during the first 2 Mc in gravimetric tests may be responsible for the absence of a run-in phase in Fig. 4, in spite of the adjustment versus soak controls. Another advantage of BF is the relative ease of particle analysis by SEM, compared to filtration, due to the confinement of captured particles to a small, well defined area (12 mm^2 compared to 531 mm^2 for the circular filter) (see Fig. 2). One may argue that BF biases to larger particles (which comprise a greater proportion of the mass), compared to filtration that biases towards the smallest particles. This, however, is not the case. While the membrane used in this study for filtration had pore size of 80 nm, i.e. smaller particles are likely to be lost, BF can capture even smaller ones (depending on the magnetic moment of the particle). In Ref. [24], for example, the applicability of BF to the capture of carbon nanoparticles was demonstrated. In addition, the main issue is by what means these particles are eventually identified. In our case, we used the same microscopic technique and the same magnifications for both filtration and BF. Hence, the results can be compared legitimately.

Some open questions related to the mechanism of magnetic labeling of PCU particles by means of $ErCl_3$ solution and BF are yet to be investigated. Firstly, it is unclear whether the magnetization is homogeneous, regardless of the PCU particle size. To answer this question, standards of known particle size distributions and particle concentrations may be necessary, but these are currently unavailable (at least, commercially) for PCU. Such standards would also allow determining the capture rate, and whether it is the same for large and small particles or for different lubricants (e.g. deion-

Table 1
Quantitative analysis of wear particles captured by either filtration or BF. The data are presented as average (range). In all cases the values for filtration were significantly different than the equivalent values for BF ($P \leqslant 0.05$).

# Cycles (1× M)		0.5	1	2	3	4	5
Filtration	Diameter (μm)	11.4 (1.0–43.9)	11.9 (2.1–48.5)	13.2 (2.2–44.2)	8.1 (1.3–64.0)	10.44 (1.7–73.3)	12.6 (1.7–63.5)
	Perimeter (μm)	42.5 (3.6–220.7)	46.5 (6.6–286.7)	53.1 (8.1–267.8)	33.8 (4.3–381.7)	41.1 (5.6–356.3)	49.3 (5.6–284.7)
	Area (μm^2)	166 (1–3015)	183 (3–1850)	192 (4–1536)	120 (1–3220)	132 (2–4215)	212 (2–3162)
	Form factor	0.75 (0.24–0.98)	0.75 (0.20–1.00)	0.73 (0.24–0.92)	0.75 (0.21–0.99)	0.72 (0.26–0.95)	0.73 (0.29–0.93)
Bio-ferrography	Diameter (μm)	16.5 (5.6–51.2)	13.6 (3.8–121.5)	17.6 (4.9–71.5)	13.3 (3.1–86.7)	13.6 (5.1–72.0)	16.6 (3.9–59.9)
	Perimeter (μm)	60.8 (16.4–228.9)	50.4 (11.6–692.1)	62.9 (14.9–383.3)	47.4 (8.9–341.8)	48.1 (14.5–291.2)	62.1 (11.7–393.3)
	Area (μm^2)	298 (24–2056)	278 (11–3252)	317 (21–4844)	212 (7–2512)	198 (20–2073)	352 (12–3953)
	Form factor	0.80 (0.28–1.11)	0.85 (0.28–1.22)	0.85 (0.34–1.21)	0.85 (0.27–1.57)	0.86 (0.40–1.22)	0.80 (0.35–1.14)

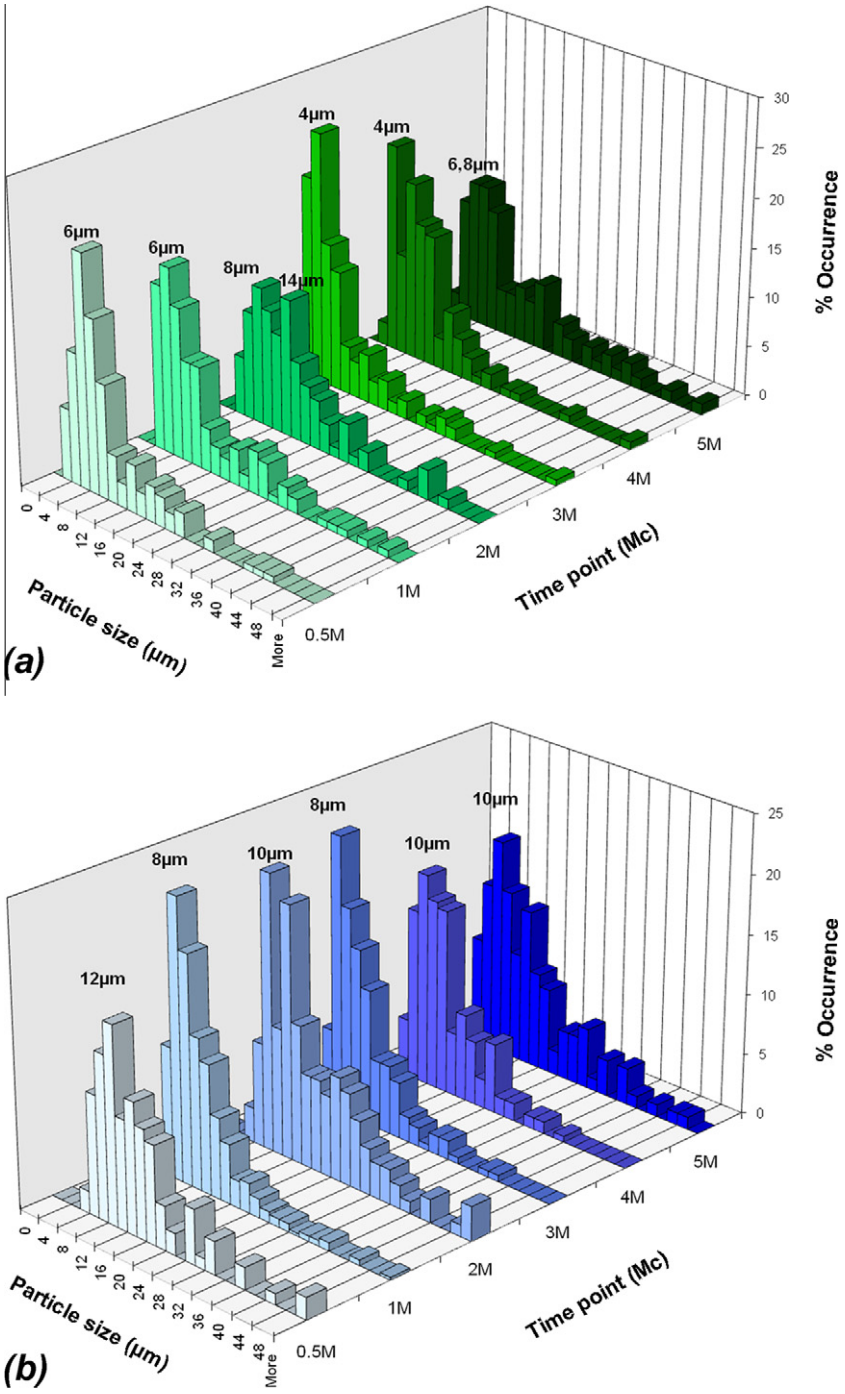

Fig. 8. Size histograms of particles isolated by (a) filtration and (b) bio-ferrography.

ized water versus bovine serum). Nevertheless, the same concentration of $ErCl_3$ used in this study (10 mM) has been used for magnetization of UHMWPE particles, including standardized ones [25]. As PCU is more polar than UHMWPE, it was anticipated that its binding to $ErCl_3$ would be sufficiently high. It should also be noted that the size distributions of captured particles in this study overlapped for BF and filtration, and that, depending on the material chemistry and magnetic moment, particles on the nanometer scale have been captured by BF [24]. One of the approaches for identifying whether magnetization and capture by BF depends on the shape and the size of PCU particles would be to filter the effluent of BF (which reaches the disposable syringes) and examine it for particles at high magnifications.

Overall, the three methods utilized in the study yielded similar results. Gravimetric and BF methods produced a wear rate of 9.9–12.5 mg Mc^{-1}, whereas filtration resulted in a wear rate of 5.8 mg Mc^{-1}. The higher sensitivity of BF compared to filtration has been reported in the case of tracking bacteria at low concentrations in water [30]. In that case, a sensitivity three orders of magnitude higher was claimed and explained in terms of the low deposition area in BF compared to filtration and the higher selectivity of BF. In addition, the number of autochthonous bacteria visually identified using BF was an order of magnitude higher than the number of colony-forming units determined from membrane filtration [30]. Larger quantities of particles were captured by BF in this study too, resulting in an accumulation of higher particle

Table 2
Wear characteristics of bearing material combinations in THR.

Bearing	Wear rate (particles Mc^{-1})	Particle size (μm)	Wear volume (mm^3 Mc^{-1})
MoM [11,32]	6.7×10^{12}–2.5×10^{14}	0.051–0.116	1–6
MoUHMWPE [11]	5×10^{11}	0.1–5	30–100
CoUHMWPE [32]	NA	0.1–5	31
CoC [32]	NA	0.009	0.05
MoPCU	10^6	8–18	5–11

mass (Figs. 4 and 6). The wear of the compliant PCU bearing was found to reach a steady rate after 2 M cycles and was therefore calculated based on the results of 2–5 million cycles.

Comparison of the results to other implant materials, in terms of the worn volume, demonstrated a lower wear rate of PCU compared to UHMWPE, lying closer to that of MoM bearings (Table 2). However, a low worn volume in itself is not the only important factor governing the long-term clinical outcome of a THR. The size and surface morphology of the wear particles and the biological response to them are also important. Recent studies have shown that wear particles generated by MoM prostheses are in the nm size range (Table 2) and, consequently, the number of particles produced in this sort of bearing may exceed the number of μm-range polymer particles of UHMWPE or PCU. Indeed, it was found that the number of PCU wear particles generated per million cycles was five orders of magnitude lower than that of MoUHMWPE, and six to eight orders of magnitude lower than that reported for MoM (Table 2). Pervious studies have also shown that particles in the 0.2–10 μm range were the most biologically active, and stimulated macrophages to produce high levels of the cytokine TNF-α [31]. While the majority of UHMWPE particles (73% by mass) have been found to lie within the 0.1–10 μm range [32], only 3.4% of the PCU wear particle mass measured in the current study was found to lie within this size range; the majority of PCU particle mass was larger in size. Interestingly, it has recently been shown by means of cell culture experiments and animal tests that even when particles in the lower (most biologically active) range are produced, PCU is less inflammatory to periprosthetic tissue and bone than cross-linked UHMWPE [33,34].

One potential limitation of direct comparison between different wear studies is the variability in testing conditions (load cycles, motions and lubricants) as well as lack of consistency in implant head sizes used in different studies. Nevertheless, by choosing to use a small (40 mm) head size configuration (high load per contact area) and complying strictly with conditions dictated by ISO-14242 hip implant testing protocol, it is believed that the current simulation conditions provide a conservative approximation. Additionally, the current estimates of the wear rate seem consistent with two recently published retrieval analysis reports, which ultimately comprise the best means of validation to the experimental setup. In the first case report, a 52/46 PCU acetabular buffer, retrieved after 10.5 months (revised for pain of unknown origin), demonstrated a wear rate of less than 1.4 mm^3 per year according to μCT analysis. The average diameter of the particles aspirated from the joint fluid and screened by SEM ($n > 100$) was found to be 2.9 μm (range: 0.5–90 μm, plus one at 200 μm) [35]. In the second case report (revised for pain of unknown origin 12 months post-implantation), the wear rate was determined to be less than 15 mm^3 per year [36].

5. Conclusions

Overall, the three methods utilized in the study to quantify the wear of PCU yielded similar results, but bio-ferrography was found to have several advantages. The gravimetric and bio-ferrography methods produced a wear rate of 9.9–12.5 mg Mc^{-1}, whereas filtration resulted in a wear rate of 5.8 mg Mc^{-1}. These results lie below values reported for polyethylene based bearings. At the same time, this study has revealed significant differences in the characteristics of PCU wear particle sizes compared to polyethylene, metal and ceramic wear debris. Larger particle sizes measured for the PCU/CoCr bearing (~13 μm), combined with lower particle generation rate ($1–5 \times 10^6$ particles Mc^{-1}) suggest that the osteolytic potential of PCU is lower than that of PE.

Conflict of interest

This research was funded by Active Implants Corporation.

Appendix A. Figures with essential colour discrimination

Certain figures in this article, particularly Figs. 1–4 and 8 are difficult to interpret in black and white. The full colour images can be found in the on-line version, at doi:10.1016/j.actbio.2010.07.011.

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