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Texturing of UHMWPE surface via NIL for low friction and wear properties

Tanu Suryadi Kustandi[1], Jian Huei Choo[2], Hong Yee Low[1,3] and Sujeet K Sinha[2,3]

[1] Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore
[2] Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore

E-mail: hy-low@imre.a-star.edu.sg and mpesks@nus.edu.sg

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Abstract

Wear is a major obstacle limiting the useful life of implanted ultra-high molecular weight polyethylene (UHMWPE) components in total joint arthroplasty. It has been a continuous effort in the implant industry to reduce the frictional wear problem of UHMWPE by improving the structure, morphology and mechanical properties of the polymer. In this paper, a new paradigm that utilizes nanoimprint lithography (NIL) in producing textures on the surface of UHMWPE is proposed to efficiently improve the tribological properties of the polymer. Friction and wear experiments were conducted on patterned and controlled (non-patterned) UHMWPE surfaces using a commercial tribometer, mounted with a silicon nitride ball, under a dry-sliding condition with normal loads ranging from 60 to 200 mN. It has been shown that the patterned UHMWPE surface showed a reduction in the coefficient of friction between 8% and 35% as compared with the controlled (non-patterned) surface, depending on the magnitude of the normal load. Reciprocating wear experiments also showed that the presence of surface textures on the polymer resulted in lower wear depth and width, with minimal material transfer to the sliding surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Total joint replacement, or arthroplasty, represents a significant advance in the treatment of painful and disabling joint pathologies [1]. Total joint arthroplasty can be performed on any joints of the body, including the hip, knee, ankle, foot, shoulder, elbow, wrist and fingers. Of these procedures, hip and knee total joint arthroplasty are by far the most common. The procedure, in general, consists of replacing the diseased or damaged joint surfaces with metal and plastic components shaped to allow continued motion of the joint parts. The most common materials used in a total hip replacement are a metal femoral head, made of cobalt–chromium, which articulates with an acetabular cup, made of ultra-high molecular weight polyethylene (UHMWPE). Similarly in the case of knee joints, the deficient and damaged tibio-femoral joint surfaces are commonly replaced with a prosthesis (implant) made of metal alloys, ceramic material or high-density plastic parts. In both cases, the implant components are designed so that metal always articulates against a polymeric material, which provides smooth movement and results in minimal wear. Although other bearing couples have been investigated during the past three decades, such as metal-on-metal or ceramic-on-ceramic total joint replacements, today metal-on-UHMWPE total joint replacements are an international standard of care for degenerative joint disorders [2].

Metal-on-UHMWPE total joint arthroplasty has thus far yielded dramatic clinical results and been found to be an effective treatment modality providing immediate pain relief and significant restoration of mobility for patients with disabilities. Despite the recognized success of total joint arthroplasty, surface wear and wear debris related periprosthetic osteolysis still represent major long-term

[3] Authors to whom any correspondence should be addressed.

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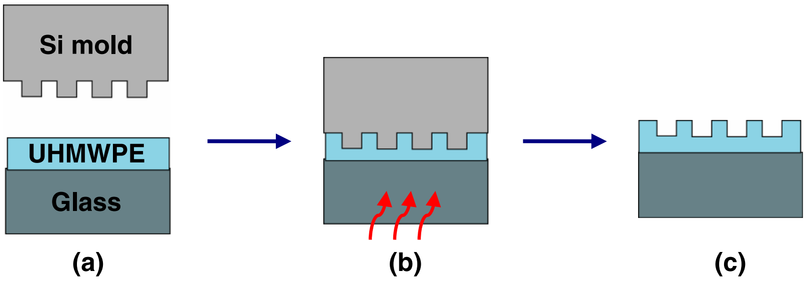

Figure 1. A schematic illustration of the basic NIL process. (*a*) Polymer is coated onto a substrate. (*b*) The imprint process was performed at an elevated temperature and pressure. (*c*) Patterned structures were transferred from the mould into the polymeric layer after de-moulding step.

complications limiting the durability of implanted UHMWPE components [3]. Polyethylene particles generated by the metal on polymer articulation are the most common inducer of osteolysis, which leads to implant loosening and eventual failure of the implant [4]. Numerous efforts have been made to solve the wear problem of UHMWPE by investigating the structure, morphology and mechanical properties of the polymer, and to develop an enhanced and more wear-resistant UHMWPE [2, 5, 6]. Recently, a micro-dimpled metal surface was reported to be effective in reducing the UHMWPE wear during a friction sliding test because the wear particles were trapped within the dimples [7]. In this study, we investigate a new approach to making low friction and wear-resistant UHMWPE in which we introduce surface texturing onto the polymer via nanoimprint lithography (NIL).

NIL is a simple, low-cost and high-resolution patterning method to produce micro- and nano-structures in a polymer. In this process, a mould containing protruding/recessed surface patterns is mechanically pressed onto the polymeric material at high temperature and high pressure. After compression and detachment of the mould, the 'negative' of the mould patterns is transferred into the polymer layer. To ensure a clean release of the mould from the patterned polymer surface after the imprinting, mould surface treatment is necessary and is typically achieved with a self-assembled monolayer (SAM) [8] or fluoropolymer deposition [9]. Figure 1 shows a schematic for the fabrication of micro- and nano-structures in a polymer using NIL. The key reason why NIL has attracted wide attention in recent years is due to its capability of patterning sub-10 nm [10] features despite its simple equipment setup and easy processing. To date the NIL method has been applied to the fabrication of various devices, including magnetic disc [11], microfluidics and microelectromechanical system (MEMS) devices [12], field effect transistors [13], photonic devices [14], and so on. The method, however, has yet to be exploited in the area of tribology in particular for the patterning of UHMWPE, the material responsible for the durability and reliability of the orthopaedic implants in total joint arthroplasty. Herein we demonstrate the use of NIL to create a polymer structure in UHMWPE and aim to further improve the knowledge of the relation between the surface texture and tribological properties of UHMWPE. The findings could be useful in the pursuit of developing a superior joint material.

2. Experimental

2.1. Sample preparation

All chemicals were purchased from Aldrich, Singapore and UHMWPE test surfaces were generously provided by 3M, Inc. Silicon master mould (1 μm gratings array with an aspect ratio of 1 : 1) was fabricated by the conventional optical lithography process. The master moulds (bare silicon and 1 μm gratings structures) were cleaned in a piranha solution (a 3 : 1 mixture of 96% sulfuric acid with 30% hydrogen peroxide) at 120 °C for 30 min, rinsed with deionized water, dried in a stream of dry nitrogen, and put in a clean oven at 100 °C for 1 h. The moulds were then exposed to oxygen plasma for 10 min in RIE I Etcher, Sirus (Trion), operated at 200 mTorr oxygen pressure, 10 sccm oxygen flow rate and a power of 100 W. The moulds were further treated with a fluorosilane release agent through an overnight vapour deposition of 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-trichlorosilane SAM. Imprinting of UHMWPE was performed using a 4 inch nanoimprinter (Obducat AB). Sheets of UHMWPE were cut slightly smaller than the mould size and placed on top of the mould. The mould and UHMWPE sheet were heated up to 130 °C, near the melting temperature of the polymer, and a pressure of 6 MPa was then applied for 10 min to let the molten UHMWPE flow slowly into the trenches of the mould. The imprint process was completed by cooling down the UHMWPE well below its melting temperature to 40 °C and releasing the pressure from the mould. The imprinted UHMWPE structures were then obtained by detaching the UHMWPE sheet from the master mould.

2.2. Characterization

High-resolution SEM imaging was carried out with a JEOL FESEM JSM-6700F. AFM imaging was performed using multimode SPM (Veeco Instruments, Inc.) in contact mode in air at room temperature. The glass transition and melting temperatures of UHMWPE were determined using a photo differential scanning calorimeter, PDSC (TA Instruments DSC Q100). A commercial tribometer (UMT-2 Universal Micro Tribometer, CETR, USA) was used to conduct linear single-pass or reciprocating friction and wear tests on the UHMWPE sample surfaces. Si_3N_4 ball of 4 mm diameter and 5 nm average surface roughness (R_a) was used as the moving counter surface. A number of ball specimens were ultrasonically

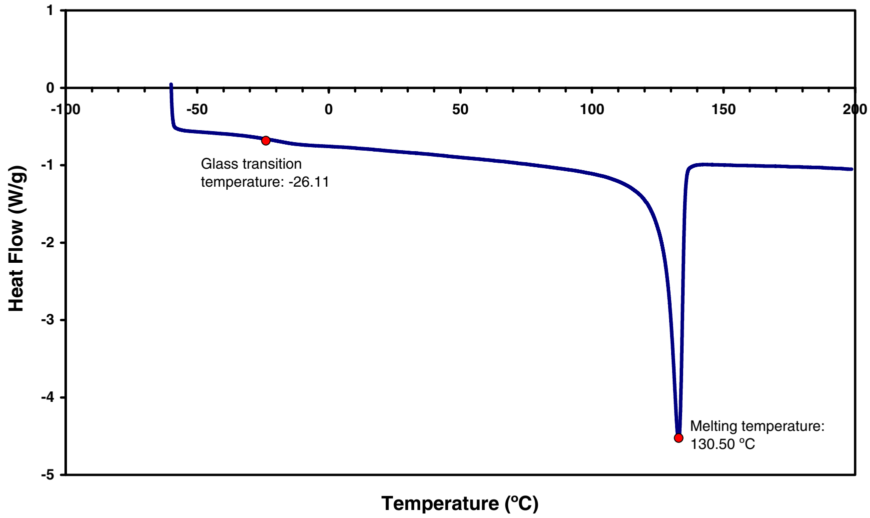

Figure 2. DSC data showing the glass transition and melting temperature for the polymer, UHMWPE.

cleaned in isopropanol followed by acetone, and then stored in a sealed glass bottle. Before each test, a ball was removed and cleaned with a lint-free cleaning swab dipped in acetone. Inspection of the ball contact area with a microscope was made to ensure that there was no particulate contaminant on the surface. The UHMWPE samples, mounted on rigid glass slide backing, were fixed onto a stationary horizontal plate with double-sided adhesive tape. Reference polymer surfaces without imprinted patterns were attached with no particular alignment to the sliding direction whereas the NIL-imprinted gratings were aligned perpendicular to the sliding direction of the counter surface. Contact loads ranging from 60 to 200 mN were used. This corresponds to maximum Hertzian contact pressures between 0.2 and 0.3 GPa (Young's modulus of 310 and 1.5 GPa and Poisson ratio of 0.22 and 0.46, for ball and UHMWPE, respectively). Single-pass sliding experiment was conducted over 1 mm distance at a rate of 1 mm s^{-1}. Reciprocating sliding experiment was conducted over 3 mm distance at a rate of 10 mm s^{-1}. Friction forces were captured and recorded for up to 8 h of testing in the reciprocating case. All tests were conducted in a class 100 clean booth environment.

3. Results and discussion

Imprinting of UHMWPE was performed at the melting temperature of the polymer at 130 °C, which was previously characterized using differential scanning calorimetry (DSC) (figure 2). Figure 3 shows scanning electron microscopy (SEM) images of the UHMWPE surface before imprinting (figure 3(*a*)) and after imprinting process using a bare silicon substrate (figure 3(*b*)) and 1 μm gratings mould (figure 3(*c*)). Excellent replication of 1 μm gratings was achieved by imprinting into UHMWPE at its melting temperature. The replication is identical to the structures of the original master, and the tops of the gratings are flat, which shows full polymer filling of the mould's cavities during imprinting. To obtain a well-defined patterned structure in UHMWPE, it is essential that a low-surface-energy release layer is applied onto the surface of the mould. Such surface treatment is especially important when the feature sizes are reduced to the nanometre-scale, where adhesion between the mould and the polymer becomes more pronounced due to the increase in the surface area.

Further examination on the top surface of the samples by SEM (insets of figures 3(*b*) and (*c*)) and atomic force microscopy (figure 3(*d*)) confirmed the presence of a distinct lamellar type of structure on the surface, which indicates crystalline regions in semicrystalline polymers [15]. The UHMWPE lamella on the surface is ∼30–50 nm thick, with inter-lamellar spacing to be approximately 50 nm. The lamellar morphology not only determines the degree of crystallinity of the samples but also influences the friction force and scratch resistance of the UHMWPE surfaces [16]. It was pointed out that the size of the lamellae is increased with slow-cooling and annealing, and decreased by quenching. The slowly cooled sample was found to have a higher degree of crystalline volume and showed a lower coefficient of friction (COF) and higher wear resistance than the quenched sample. These findings were attributed to the increase in storage modulus and to the mechanical reinforcement due to the formation of larger lamellae [17]. Clearly, in the NIL process the semicrystalline polymer undergoes slow and gradual thermal processing upon which the chains in amorphous regions disentangle, followed by the tilting and slipping of the chains in crystalline regions. While it would be interesting to investigate the effects of nanoimprint on the morphology of the material, the emphasis of this paper is on the tribological properties of UHMWPE. In order to eliminate any possible morphological changes caused by the nanoimprint process, a controlled sample (non-patterned) was prepared by imprinting the UHMWPE surface using a bare silicon substrate (this experiment simulates the processing history of nanoimprint without creating a surface texture). The tribological performances of this sample were subsequently compared with those of the patterned sample (imprinted using 1 μm gratings structures); with all other processing methods being identical so that conclusions drawn can be directly

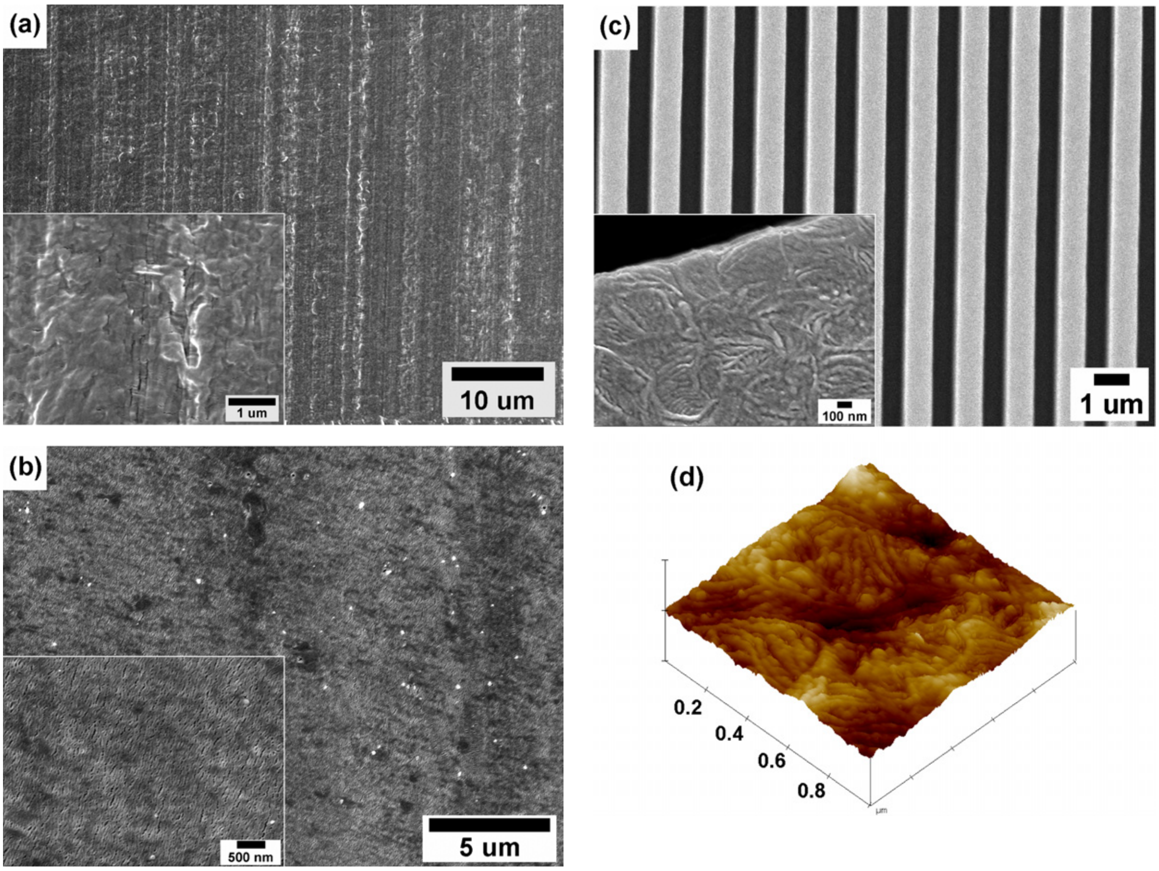

Figure 3. Scanning electron microscope (SEM) images of UHMWPE surfaces (*a*) before imprinting and after imprinting by (*b*) bare silicon substrate and (*c*) 1 μm gratings mould (inset shows the surface morphology of UHMWPE comprising fibrils-like structures). (*d*) AFM image of UHMWPE surfaces imprinted by the bare silicon substrate or 1 μm gratings mould.

correlated with the difference in surface textures between the samples.

Figure 4(*a*) shows a typical friction versus sliding-distance plot obtained in the single-pass experiments for both the non-patterned (controlled) and the patterned UHMWPE surfaces. The initial static friction of the patterned surface was found to be significantly lower than that of the controlled surface, with peak values observed at ∼60 mN and ∼140 mN for the patterned and controlled samples, respectively. This could be attributed to the lower initial contact surface area on the patterned sample, as suggested by Yoon *et al* [18]. It can be approximated that the area of contact between the control surface and the patterned surface is half of the contact area in the controlled sample. After the initial static friction response, friction values dropped dramatically for both samples and levelled off at around ∼30 mN (patterned) and ∼55 mN (controlled). To confirm the repeatability of the results, friction experiments were also performed at various normal loads, ranging from 60 to 200 mN. Figure 4(*b*) shows friction force as a function of normal load for both patterned and controlled UHMWPE surfaces. The friction force was calculated by averaging the single-pass dynamic friction values plotted in figure 4(*a*). For both the samples across scales the friction force increased with an increase in normal load. A lower COF was clearly observed on the patterned sample as compared with the controlled sample due to the reduction in effective contact area between two surfaces in the presence of textures. To assess the long-term tribological performance of the patterned and controlled samples, the UHMWPE surfaces were exposed to a reciprocating wear test for a total time of 3600 s, which corresponds to 6000 cycles of reciprocation, under the load of 200 mN. Figure 4(*c*) shows the COF plotted against time in seconds. The patterned surface consistently showed lower COF and less fluctuation as compared with the controlled surface (∼0.18 versus ∼0.3).

A longer duration of reciprocating wear test was conducted for 8 h, under the normal load of 200 mN, to determine the wear resistance of the patterned UHMWPE. It was noted that, even after 48 000 cycles of dry sliding on the imprinted surface, the imprinted features were still present with evidence of very low wear on the patterned sample, as shown in figure 5(*a*). The grating structures experienced a gradual deformation along with the sliding cycles and were flattened after an extensive sliding process. The top surface of the UHMWPE material was sheared and reflowed to fill up the trenches. An enhanced wear resistance of the patterned UHMWPE was further confirmed by comparing the amount of material transfer with the silicon nitride ball after the reciprocating wear experiments. Figures 5(*b*) and (*c*) show the optical images of the surface of the silicon nitride ball after extensive sliding on the patterned and controlled UHMWPE surfaces, respectively. When the silicon nitride ball slid against

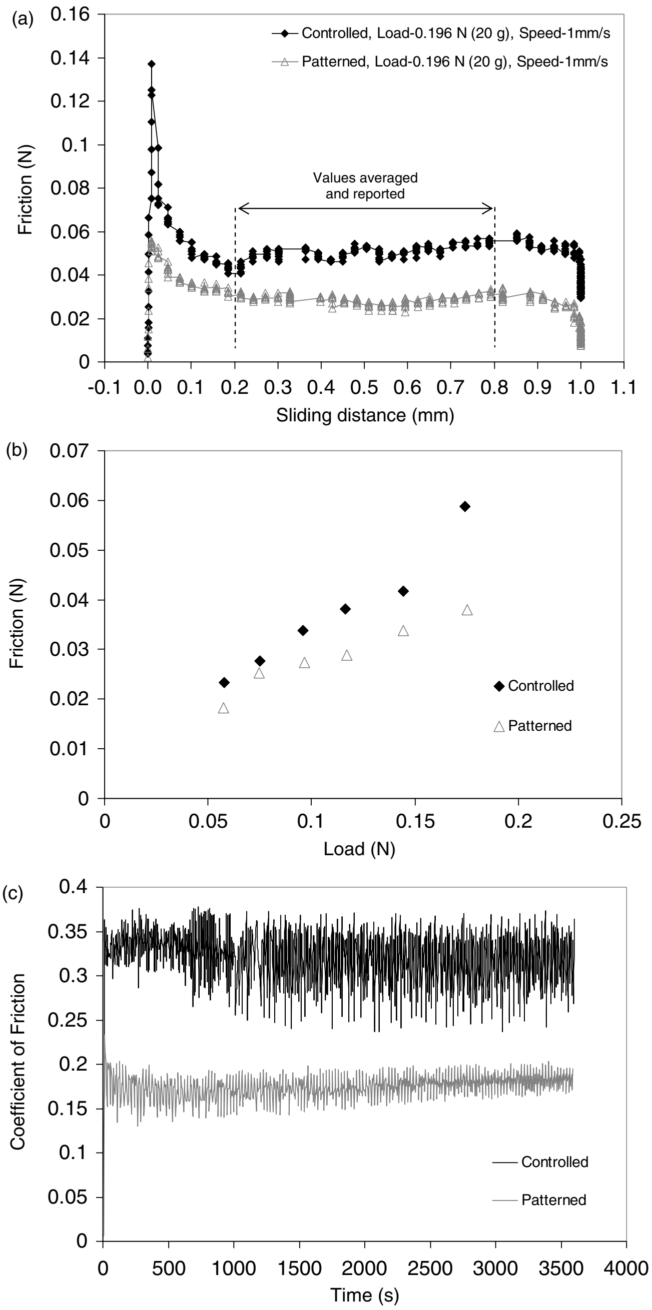

Figure 4. (*a*) Single-pass friction plots for controlled (non-patterned) and patterned UHMWPE surfaces. Test conditions used: 200 mN, 1 mm s^{-1} sliding speed, 1 mm distance. (*b*) Single-pass friction results of UHMWPE surfaces imprinted using the bare silicon substrate (diamond data points) and 1 μm gratings mould (triangle data points). (*c*) Reciprocating friction test on controlled (upper plot) and patterned (lower plot) UHMWPE surfaces. Test conditions used: 200 mN, 10 mm s^{-1}, 3600 s.

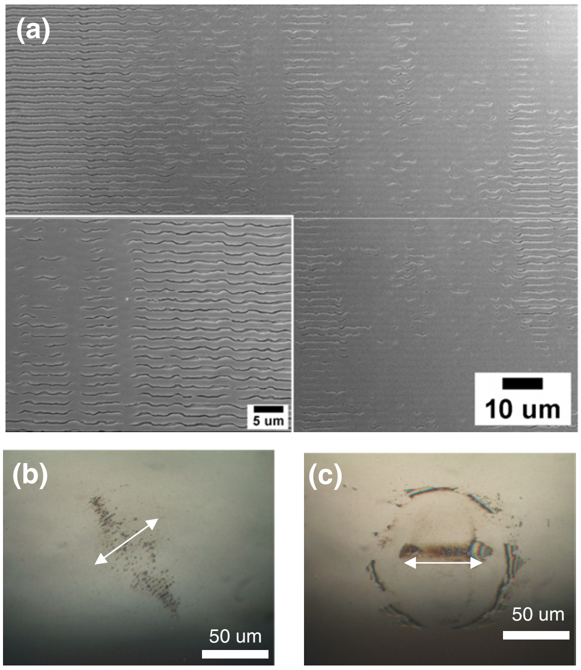

Figure 5. Results from an 8 h reciprocating friction test (∼48 000 cycles) on the patterned UHMWPE surface. Test conditions used: 200 mN load, 10 mm s^{-1} sliding speed, 3 mm sliding distance, 8 h duration. (*a*) SEM image of the deformed UHMWPE gratings structures after the friction test. In the inset of (*a*) is shown a slightly magnified view. (*b*) and (*c*) Optical images of the debris transfer on the sliding Si_3N_4 counter surface after the friction test on a patterned (*b*) and a controlled surface (*c*), respectively. Arrow indicates the sliding direction of the friction tests.

the patterned sample, a very minimal material transfer from the UHWMPE surface was found on the ball surface, indicating an excellent wear resistance of the polymer after the extensive sliding process. On the other hand, in the controlled sample case, polymer debris was transferred onto the ball surface in the centre and around the periphery of the contact area between two surfaces. It is noted that the periphery has a diameter of approximately 100 μm, which closely corresponds to the calculated Hertzian contact radius of 50 μm at 20 mN of load. This type of lumpy material transfer from the controlled sample to the counter ball surface has a negative effect on increasing friction due to the high area of contact and the nature of polymer-on-polymer friction mode. When a layer of polymer slides over another layer of polymer, there tends to be entanglement of polymer molecules from both surfaces (as opposed to a metal on polymer contact), hence resulting in a higher friction [19].

4. Conclusions

NIL has now emerged as a fast and relatively easy technique capable of fabricating micro- and nano-structures in a polymer. We have shown that, via NIL, patterned structures can be prepared onto the surface of a low friction and low wear polymer, UHMWPE, which further reduce the COF (between 8% and 35% reduction, depending on the normal load) and enhance the wear resistance of the polymer. The friction and wear experiments presented in this paper were conducted at a much more severe load (200 mN versus 3 mN), a higher sliding rate (10 mm s^{-1} versus 1 mm s^{-1}) and for a longer duration (8 h versus 5 min) than those presented in the published work [18]. Despite such severe experimental conditions, the patterned UHMWPE survived a long duration of dry sliding against the silicon nitride ball and there is no debris formation on the counter surface. We are currently exploring the possibility of introducing nanoscale lubricant, such as polyperfluoropolyether (PFPE), onto the patterned UHMWPE for much greater enhancement of wear life.

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