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Development of Multifunctional Liquid-infused Materials by Printing Assisted Functionalization on Porous Nanocomposites

Wenqing He, Peng Liu, Jieke Jiang, Meijin Liu, Hualin Li, Jianqiang Zhang, Yan Luo, Hon Yeung Cheung and Xi Yao

We reported porous polymer nanocomposite with polar and non-polar components which are suitable for both loading functional molecules and lubricating as liquid-infused materials. By printing functional inks into the nanocomposites, a couple of unique features were demonstrated on the developed multi-functional liquid-infused materials.
Development of Multifunctional Liquid-infused Materials by Printing Assisted Functionalization on Porous Nanocomposites

Wenqing He\textsuperscript{a}, Peng Liu\textsuperscript{b}, Jieke Jiang\textsuperscript{a}, Meijin Liu\textsuperscript{a}, Hualin Li\textsuperscript{a}, Jianqiang Zhang\textsuperscript{a}, Yan Luo\textsuperscript{b}, Hon Yeung Cheung\textsuperscript{a}\textsuperscript{*} and Xi Yao\textsuperscript{a,ac}

We report stable and mechanically robust bi-component nanocomposites capable of post modification for the development of multifunctional liquid-infused materials. The non-polar polymer network provides mechanical robustness and compatibility to mineral oils for lubrication and surface slipperiness, and the polar nanoparticles improve loading capacity with polar molecules for functionalization. Besides of the surface slipperiness, we successfully integrate desirable physicochemical properties into the nanocomposite by printing specific inks on the nanocomposites. Unique properties including controlled surface slipperiness, self-reporting on the loss of liquid repellency, sensing the temperature of contacting liquids are demonstrated on the printed nanocomposites with lubrication treatment. Our design strategy could be applied in the development of multifunctional liquid-infused materials for applications in anti-fouling coating, food/medical packaging, smart windows and sensors.

Introduction

Introducing a liquid into a porous solid would result in a dynamic fluid interface with a super-slippery character. Liquid-infused materials (LIMs) with extreme surface slipperiness have great impact of technical implications in self-cleaning\textsuperscript{1} and oil-water separation,\textsuperscript{2, 3} droplet transportation,\textsuperscript{4-7} anti-corrosion\textsuperscript{8, 9} and anti-icing\textsuperscript{10, 11} coating, anti-fouling\textsuperscript{12-14} and those in biomedical fields.\textsuperscript{15-19} To meet the growing requirements in versatile real-world applications, the next-generation LIMs are favorable to have appropriate combinations of surface slipperiness and specific physicochemical properties such as optical tunability, mechanical robustness, chemical and biological activities to achieve multifunctionality and synergize for optimal performance. For example, LIMs made from lubricant swollen polymers or elastomers could bring together surface slipperiness and desired functionality from the polymers or elastomers such as stimuli-responsiveness, shape memory or even self-healing which could largely extend their application scope.\textsuperscript{20-27} Moreover, LIMs developed from photocatalytic oxides coatings could combine the surface slipperiness and photocatalytic activity for improved self-cleaning and anti-fouling.\textsuperscript{28} One challenge in designing multifunctional LIMs lies in the developing methods that allow customizing physicochemical properties of the lubricant-infusing substrates while keeping the surface slipperiness unaffected, or vice versa. Post modification methods represent a typical strategy to modify or tune the physicochemical properties after fabrication.\textsuperscript{29, 30} Current modification methods on liquid-repellent materials are mainly based on surface chemical modifications which are molecular-dependent and rely on specific chemical reactions, such as those in the reactive superhydrophobic surfaces\textsuperscript{31, 32} and reactive “liquid-like” surfaces.\textsuperscript{33, 34} Although materials from non-polar and chemical-inert molecules are still the primary choices in the development of LIMs coatings which are resistant for chemical modification, involving more functional/polar molecules into the LIMs coatings could help improve their performance. For example, bio-active molecules, such as triclosan and quorum sensing inhibitors have been loaded into the porous substrates before lubrication, which could then diffuse gradually through the lubricant layer into the surrounding media for long-term anti-biofouling.\textsuperscript{35, 36} However, most chem- or bio-active agents are polar molecules and have poor compatibility with the substrates made from non-polar molecules, resulting in limited loading efficiency, and would thus suppress the performance of the multifunctional LIMs coatings. Nevertheless, to develop LIMs capable of post modification with desirable tunability for multifunction remains challenging.

Herein, we reported a strategy of preparing multifunctional liquid-infused materials via printing assisted post-modification on porous polymer nanocomposites. To allow efficient post-modification, porous polymer nanocomposites with both polar and non-polar components were developed and used as...
substrates on which polar inks with various properties could be printed for functionalization (Fig. 1a). Unique properties including control of surface slipperiness, self-report of wettability change, and stimuli-responsiveness were therefore demonstrated after lubrication, resulting in multifunctional liquid-infused materials. Briefly, the porous polymer nanocomposites were fabricated from a thermally induced phase separation process\textsuperscript{37-39} in the blending and extruding of ultrahigh-molecular-weight polyethylene (UHMWPE) and SiO\textsubscript{2} nanoparticle mixtures followed by a thermal-compression process to obtain flat films. In this system, the hydrophobic UHMWPE was selected as the non-polar component due to its biocompatibility, excellent chemical resistance and mechanical robustness.\textsuperscript{40, 41} The hydrophilic SiO\textsubscript{2} nanoparticles were added as the polar component which could induce the formation of pores and surface microstructure of the fabricated porous film, and more importantly, they could improve the loading capacity of polar molecules/inks in the porous nanocomposites. Printing methods were used to post modify the porous substrate before lubrication due to the convenience in ink selection and the high precision in surface patterning.\textsuperscript{42} Here, all the raw materials and technologies are widely used in industry and the fabrication process is cost effective, which could satisfy potential large scale manufacture and applications. Furthermore, the UHMWPE/SiO\textsubscript{2} composites are widely used in paper and packaging industry, and we believe their innovative application as multifunctional LIMs could further facilitate their performance in related fields.

Results and discussion

Fabrication and ink-jet printing performance of UHMWPE/SiO\textsubscript{2} Nanocomposites

Since the UHMWPE and SiO\textsubscript{2} have distinct surface wettability and polarity, their weight ratio would affect the microstructure of the as-prepared nanocomposites and thus the ink-retention after printing. Surface morphology on representative samples with varying weight percentages (wt) of SiO\textsubscript{2} nanoparticles, 0 wt%, 3.5 wt% and 7 wt% (termed as S0, S3.5, and S7, respectively) were presented in Fig. 1b. Indeed, the micropores were densely and uniformly distributed in the S3.5, and the pore size and distribution became more random for S7. Detailed comparison on the nanocomposites of various compositions could be found in Fig. S1. A standard printing test was performed on the as-prepared substrates using a commercial inkjet printer (Fig. S1). The printed characters on S0 were blurred and beyond recognition, and the printing quality was improved substantially on the S3.5 substrate. When further increasing the SiO\textsubscript{2} content, the printing quality would be suppressed as in the S7 and S10 substrates. The zoom-in observation on the printed pattern showed that the lateral spreading and the penetration of the polar ink varied on different nanocomposites (Fig. 1c-d). The ink droplets could penetrate slightly in the S0 substrate and stained on the surface with gel-like appearance which could be wiped away easily, indicating the poor compatibility between the non-polar UHMWPE and polar inks. In comparison, ink droplets penetrated more deeply into the S3.5 and S7 substrates due to the strong affinity provided by the polar SiO\textsubscript{2} nanoparticles. The lateral spreading and the penetration depth for S7

![Fig. 1](image-url)
substrate was more random than that of S3.5 substrate, which might be attributed to the phase-separation induced severe agglomeration of SiO\(_2\) on the nanocomposite (Fig. S2). Actually, the penetration of the ink inside the nanocomposite determined the amount of materials that could be effectively loaded into the nanocomposite through the printing methods.

**Lubrication of UHMWPE/SiO\(_2\) Nanocomposites**

The addition of SiO\(_2\) nanoparticles could improve the tensile strength of the nanocomposite (Fig. S3). And they showed excellent stability under various conditions. As exemplified on the S3.5 sample, the surface hydrophobicity was unaffected and water contact angle (WCA) was maintained around 110° under various treatments, for example, immersion in 98 wt% sulfuric acid and 25 wt% ammonia solution for 10 days, continuous UV irradiation and thermal treatment (in 100 °C oven) for 10 days (Fig. S4). To choose a suitable lubricant with a minimal evaporation rate and good compatibility to the nanocomposites, three kinds of lubricants, including mineral oils of 68 cSt and 10 cSt viscosity, and silicone oil of 10 cSt viscosity were selected for comparison. After lubricant overcoating, the superfluous oil layer was removed by spinning at 1000 rpm for 2 min to obtain LIM samples. Shear stability tests were performed on the lubricant treated samples by using a water stirring bath. Fig. 2a illustrated the experiment setup. Briefly, the lubricated sample (red) was immersed in water bath, in which a magnetic bar stirred at 400 rpm to apply a continuous shear flow on the sample surface. The contact angle hysteresis (CAH) of the sample was measured.

![Fig. 2 Stability, Liquid repellency and anti-biofouling property of the lubricated nanocomposites. (a) Schematic diagram of shearing-stability test in a stirring water bath. (b) Shear stability test of the nanocomposites infused with different lubricants. (c) Thermal stability of LIM-S3.5 by using 68 cSt mineral oil as the lubricant. (d) Images showing the sliding of test liquids on the 68 cSt mineral oil lubricated nanocomposite. Typical SEM images on the bacteria coverage on the S3.5 sample before (e) and after (f) wash by saline solution S3.5, and on the LIM-S3.5 sample before (g) and after (h) wash by saline solution. Scale bar: 5 µm. (i) Quantitative study on the bacteria adhesion of S3.5 and LIM-S3.5 samples through crystal violet staining. Result from S3.5 was recommended as 1 for normalization and comparison.](image-url)
after various stirring periods of time. Indeed, all the samples showed increased CAH after the shear flow indicating the loss of the lubricant, but the sample coated with the 68 cSt mineral oil showed the best stability due to the enhanced viscosity and better compatibility with UHMWPE (Fig. 2b). Moreover, the 68 cSt mineral oil showed minimal evaporation rate, and brought high thermal stability to the lubricated sample (Fig. 2c and S5). Considering the overall performance of the nanocomposite and lubricant, the 68 cSt mineral oil lubricated S3.5 nanocomposite was selected as representative sample for LIM (termed as LIM-S3.5) in following tests and demonstrations.

Evaluation on the stability of mineral oil on the nanocomposite

The contact angles of water and mineral oil on the nanocomposite were measured to determine whether the combination of nanocomposite and mineral oil met the following criteria of the lubricant infused materials by Wong et al.1,44

\[
\Delta E_1 = R(\gamma_{oA} \cos \theta_0 - \gamma_{wA} \cos \theta_w) - \gamma_{wO} > 0
\]

\[
\Delta E_2 = R(\gamma_{oA} \cos \theta_0 - \gamma_{wA} \cos \theta_w) + \gamma_{wA} - \gamma_{oA} > 0
\]

where \( \Delta E_1 \) and \( \Delta E_2 \) indicate the working conditions for maintaining a stable lubricant infused material, \( \gamma \) is the interfacial tension between two phases, designated by the subscripts \( w \) (water), \( o \) (mineral oil), and \( a \) (air), and \( \theta_0 \) and \( \theta_w \) are the contact angles of mineral oil and water on the nanocomposite in air. \( R \) is the roughness factor of the nanocomposite, which is defined as the ratio of the solid–liquid area \( A_w \) to its projection on a flat substrate \( A_r \), which can be calculated by water contact angle for a rough surface and a smooth surface.1,45

\[
R = \frac{A_{SL}}{A_F} = \frac{\cos \theta_w}{\cos \theta}
\]

where \( \theta \) is 101.5 ± 1.2° on the flat UHMWPE substrate. \( \gamma_{oA} \) and \( \gamma_{wA} \) were adopted from literature.46

The surface/interface tensions of mineral oil and water, and their contact angles on the nanocomposite 3.5 were listed in Table 1. And the results showed the LIM-S3.5 met the criteria of the lubricant infused materials, indicating that LIM-S3.5 was consisted of a porous nanocomposite and a lubricant layer.

<table>
<thead>
<tr>
<th>( \gamma ) (mN/m)</th>
<th>( \theta ) (°)</th>
<th>( R )</th>
<th>( \Delta E_1 )</th>
<th>( \Delta E_2 )</th>
<th>( S_{oA} )</th>
</tr>
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<tr>
<td>28</td>
<td>72</td>
<td>49</td>
<td>0</td>
<td>107-115</td>
<td>1.5-2.3</td>
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<tr>
<td>29</td>
<td>60</td>
<td>50</td>
<td>-5</td>
<td>119-181</td>
<td>-5</td>
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The spreading coefficient can be applied to describe the cloaking:47

\[
S_{oA} = \gamma_{wA} - \gamma_{wA} - \gamma_{oA}
\]

\( S_{oA} > 0 \) implies that the lubricant oil will cloak the contacting water droplet and that the lubricant oil will loss and deplete more easily through the continuous sliding of water and the evaporation of oil, whereas \( S_{oA} < 0 \) indicates otherwise. For LIM-S3.5, \( S_{oA} = -5 \) (Table 1), so the mineral oil was stably encapsulated by the porous nanocomposite.

Liquid repellency and antibiofouling property

Similar to other reported LIMs, the LIM-S3.5 exhibited excellent repellency to water, a couple of organic solvents, food and medical fluids which are immiscible to the overcoated mineral oil, as shown in Fig. 2d. The anti-biofouling property of LIM-S3.5 was demonstrated by using \( P. \ aeruginosa \) as a model system. The samples of bare S3.5 and lubricated LIM-S3.5 were immersed in the culture medium of \( P. \ aeruginosa \) for 48h to allow bacteria adhesion. The densely covered bacteria cells on the S3.5 sample could not be washed out with saline, indicating strong bacteria adhesion (Fig. 2e-f). In comparison, only few bacteria cells were found on the surface of the LIM-S3.5 sample, and those cells could be easily removed under gentle saline washing, indicating reduced bacteria adhesion (Fig. 2g-h). Quantification study was carried out by crystal violet staining on the bacteria adhered samples followed by absorbance measurement at 590 nm. As shown in Fig. 2i, the LIM-S3.5 sample after gentle saline washing indicated a 98% decrease on the bacteria adhesion comparing to the S3.5 sample. The toxicity screening results indicated that the mineral oil and LIM-S3.5 had no inhibition on bacteria growth and the non-adhesion of bacteria on LIM-S3.5 was attributed to the mineral oil layer worked as a slippery interface between nanocomposite and bacteria (Fig. S6).

Resistance to abrasion

Abrasion resistance is very important in the real-world applications of liquid repellent coatings. The printed nanocomposites also exhibit mechanical robustness in abrasion test. Here, we evaluated the abrasion resistance for printed nanocomposites (termed as Print-S3.5) with and without lubrication. The Print-S3.5 was cut into two parts. The top part (Printed-S3.5) was the control without lubricant, and the bottom part was infused with mineral oil (LIM-Printed-S3.5). The samples were abraded longitudinally and transversely in each cycle (Fig. 3a). After about 300 cycles, the abraded area of Printed-S3.5 became blurred (Fig. 3b) and superhydrophobic owing to the increase of roughness (inset figure in Fig. 3c). The bottom part, however, kept nearly the same appearance after abrasion for 300 cycles and had nearly the same WCA during abrasion for 1000 cycles. Accordingly, water can roll off easier and easier on abraded Printed-S3.5 with the process of abrasion. As for the LIM-Printed-S3.5, the sliding angle changed very little. Both the WCA and SA changed very little on the lubricated nanocomposite because the lubricant flowed back and reconfigured on the roughen sample.4

Table 1 Surface/interface tensions of mineral oil and water, and their contact angles on the nanocomposite S3.5 substrate.

<table>
<thead>
<tr>
<th>( \gamma ) (mN/m)</th>
<th>( \theta ) (°)</th>
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<td>-5</td>
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Fig. 3 The LMs showed better resistance to abrasion. (a) Schematic diagram of the abrasion process. (b) Images of Printed-S3.5 (up) and LIM-Printed-S3.5 (bottom) during the abrasion process. (c) WCA of Printed-S3.5 and LIM-Printed-S3.5 during the abrasion process; the inset SEM images showed the increase of roughness introduced by abrasion. (d) The sliding angles of printed S3.5 and LIM-Printed-S3.5 during the abrasion process. Scale bar: (b) 1 cm; (c) 100 µm.

Fig. 4 Different amount of hydrochromic inks were loaded to tune the surface wettability and slipperiness of LIM-Printed-S3.5. (a) Schematic illustrated the affinity evaluation of lubricant to substrates with various ink coverage. A spinning method was used to induce lubricant depletion. (b) Images of the substrates printed with different amounts of inks followed by lubrication. (c) Confocal microscope images on the oil layer retained on the nanocomposite S3.5 substrates after spinning tests. Green - mineral oil, red - printed ink, yellow - overlap of the two colors, respectively. (d) Quantification on the thickness of oil layer and sliding angle for corresponding samples loaded with different amount inks. (e) Images showed the sliding of dyed water on the sample printed with moderate inks. (f) Water droplets were pinned on a sample printed with excess inks. Scale bar: (b) 2 mm; (c) 40 µm; (e) and (f) 5 mm.
Printing regulated surface slipperiness

Besides of the normal commercial ink used above, which almost didn’t affect the surface slipperiness via normal ink-jet printing (Fig. S7), we also loaded inks with specific properties into the nanocomposites to realize various functions, for example, controlled surface slipperiness, self-reporting on the loss of liquid repellency, sensing the temperature of contacting liquids. All the inks used here are commercial-available (Fig. S8). We first loaded hydrochromic inks into the nanocomposite to tune the surface wettability and slipperiness. Because the inks are composed of polar and hydrophilic molecules which have less affinity to the non-polar mineral oil, we hypothesized that the ink coverage would affect the stability of the overcoated mineral oil on the printed nanocomposites which could be accessed via the spinning method (Fig. 4a), in which the centrifugal force could help remove the unstable lubricant.38 By screen printing hydrochromic ink on the S3.5 substrate with varying loading amount from 5 g/m² to 35 g/m², the substrates turned into vivid blue with enhanced saturation (Fig. 4b). By labelling the printed ink and oil layer with different dyes, distribution of the retained oil layer could be investigated by confocal microscopy. As shown in Fig. 4c, the retained oil layer on the S3.5 with 5 g/m² ink-loading had the largest thickness around 20 μm. With the increase of ink loading amount, the retained oil layer got thinner, indicating the reduced affinity and weak stability of mineral oil on those substrates. Specifically, the retained oil could not form a uniform layer to cover the S3.5 printed with 35 g/m² inks. This is caused by the incompatibility between the polar ink and the non-polar mineral oils. With the increase of ink loading, the ink covered area showed reduced affinity to the mineral oil, and thus the overcoated oil layer will rupture under the disturbances of spinning (Fig. 4a and S8). Following sliding angle measurements confirmed the loss of the lubricant on those surfaces that the water sliding angle decreased with the increase of ink loading (Fig. 4d-f).

Self-report of the surface slipperiness

Following we demonstrated the self-reporting on the change of surface slipperiness on the printed substrates. The surface slipperiness and the liquid repellency of LIMs could be lost when the overcoated lubricant could not be maintained on the substrate under different disturbances, for example, evaporation and shear flow. It is critical to monitor the longevity of LIMs in real-world applications such as anti-fouling and heat-transfer, so that users could replenish the lubricant or repair the materials to refresh the surface slipperiness. There are a few reports demonstrated the self-report property on the surface slipperiness via mechanical responsiveness,4-6 yet systems that could report the depletion of lubricant and the loss of slipperiness are very rare. By printing hydrochromic inks onto the nanocomposites, the rapture of overcoated lubricant and thus the change of surface slipperiness could be reported due to the water assisted color change of the printed ink (Fig. 5a). Fig. 5b exhibited a proof-of-concept demonstration of self-reporting. Appropriate amount of hydrochromic inks were screen printed on S3.5 with a “City University of Hong Kong” pattern. The ink loading amount was ~ 5 g/m² so that a stable overcoated lubricant layer could be retained on the printed substrate. Then the lubricated sample was put in the water stirring bath to accelerate the depletion of mineral oil. Within 90 mins, the blue pattern got blurred, indicating the gradual rapture of the oil layer. After 10 h, the whole blue pattern vanished and turned into colorless, indicating the penetration of water into the substrate and thus the loss of the surface slipperiness. And after drying and then replenishment with mineral oil, the LIMs can be reused.

Indicate the temperature of contacting liquids

By loading thermochromic ink, our system can indicate the temperature of contacting liquids. As a proof-of-concept demonstration, the thermochromic ink which will turn from red to colorless when its temperature is above 30 °C, was printed onto the S3.5 nanocomposite. On the sample lubricated with mineral oil, namely, LIM-Printed-S3.5, hot (dyed green, 60 °C) and cool (dyed yellow, 20 °C) water droplets could slide readily (Fig. 6a-b). The substrate on the sliding pathway of the hot droplet turned into colorless due to thermal responsiveness of the printed thermochromic ink (Fig. 6a). In comparison, the contact and sliding of the droplet with lower temperature would not trigger the color change on the printed thermochromic ink (Fig. 6b). The thermal induced color change is reliable and can be repeated for many times, which could be useful in the development of non-fouling sensors. As demonstrated in Fig. 6c, the printed pattern “COOL” on the LIM-Printed-S3.5 sample disappeared when the substrate was immersed in hot water and appeared when the substrate was immersed in cold water. During the whole process, the surface
of the substrate was not contaminated by the dyed water solutions (supporting video). Moreover, inks printed in nanocomposite could be removed and erased by simple sonication in ethanol or acetone (Fig. 6d-e). Such cleaning process would not affect the microstructure of the nanocomposite and thus the printing resolution, allowing the reuse/recycle of the nanocomposites in ink printing and surface patterning.

Conclusions

In summary, we reported the development of UHMWPE/SiO$_2$ nanocomposites capable of post modification for the development of multifunctional liquid-infused materials. The nanocomposite is composed of both polar and non-polar components, making them suitable both in loading polar molecules for post modificationfunctionalization and surface lubrication for liquid repellency. The nanocomposites are stable and mechanically robust, and they could repel various fluids after lubrication. More functions could be integrated by loading different molecules. By using printing methods, we successfully integrate desirable physicochemical properties into the printed nanocomposites in ink printing and surface patterning.

Experimental

Materials

UHMWPE (number-average molecular weight ~2,000,000) was purchased from Shanghai Lianle Chemical Industry Science and Technology Co., Ltd., China. Mineral oil (Non-polar alkane mixtures of C15 to C40, 68 cSt or 10 cSt viscosity,) was obtained from Sinopec. SiO$_2$ (hydrophilic fumed silica; product code: A200; average primary particle size: 12 nm, Fig. S10) was supplied by Degussa. UHMWPE, mineral oil and SiO$_2$ were all industrial grade. Coumarin 6 (98%), Nile red, which stained mineral oil and the ink deposit respectively for confocal observation were purchased from Sigma-Aldrich. Food coloring (McCormick) was used to aid visualization in videos and images. The hydrochromic ink (HIC, copper(II) chloride base) and thermochromic ink (238C, the core contents are thermochromic microcapsules with heat sensitive leuco-dye color developer and temperature controllers) were purchased from Shanghai Hengyuan Macromolecular Materials Co., Ltd. and Taipei New Prismatic Enterprise Co., Ltd. respectively.

Preparation of UHMWPE/SiO$_2$ nanocomposites

Porous UHMWPE/SiO$_2$ nanocomposites were prepared using thermally induced phase separation (TIPS) approach.
UHMWPE powder and SiO$_2$ nanoparticles were first blended with 68 cSt mineral oil using a digital dual-range mixer (RW20, IKA, Germany) and mixed at room temperature with 500 rpm for 2h. The mass fraction of mineral oil in all mixtures was fixed at 75 wt% which served as porogen in the phase-separation process. The mass ratio of SiO$_2$/UHMWPE was variable (1/99−10/90), thus the content of SiO$_2$ in the solid nanocomposite was 1 wt%, 2 wt%, 3.5 wt%, 5 wt%, 7 wt%, 10 wt%. The premixed mixture was poured into a conical twin-screw extruder at 220 °C in N$_2$ atmosphere with extrusion speed of 10 rpm. The extruded blend was cut into the master batch by using a plastic granulator followed by hot-pressing at 200 °C and 10 MPa for 15 min to obtain flat membranes with 400 μm thickness. The mineral oil could be washed out by ethanol bath and recycled for further nanocomposite fabrication or lubrication.

Characterization

The surface morphology of the nanocomposite was observed by using scanning electron microscope (SEM) (Philips XL30CP). The samples were coated with gold in a rarefied argon atmosphere (20 Pa) using an Emitech K550 Sputter Coater, with a current of 12 mA for 50 s. Sectioned thin films of the nanocomposites (~50 nm) were prepared through cryotomy and then observed by transmission electron microscopy (TEM) (FE/Philips Tecnai 12 BioTWIN). The element distribution and percentage of UHMWPE/SiO$_2$ nanocomposites were analyzed by energy dispersive spectroscopy (EDS) (Oxford Instruments INCA Energy 200). The thermal property of samples was measured by thermal gravimetric analysis (TGA) at a heating rate of 10 °C/min. The tensile strength of the nanocomposites was tested with an Instron machine at room temperature with a tensile speed at 5 mm/min. The initial gauge length and width were 50 mm and 10 mm respectively. Static water contact angle (WCA), sliding angle (SA), contact angle hysteresis (CAH) were measured with a customized system. Each WCA, SA or CAH value was averaged from five measurements made at different positions on the nanocomposite surface. The optical images were obtained on a tilted glass platform with a Nikon D5500. The brightness and contrast of optical images were enhanced for clarity. Printing on UHMWPE/SiO$_2$ nanocomposites was performed by commercial-available ink-jet printer (L801, Epson, Japan) with original ink. Besides, two additional inks including the thermochromic ink and hydrochromic ink were also for demonstration. The cross-section of printed samples was polished and then the ink penetration phenomenon was observed by metallurgical microscope (Olympus PMG3).

Sandpaper abrasion test

The sample faced up sandpaper (grit no. 220). Sandpaper under a 500 g weight was moved for 3 cm by an external drawing force, the sample was rotated by 90° (face to the sandpaper) and then moved for 3 cm along the journey (Fig. 4a). This process is defined as one abrasion cycle, which guarantees the surface is abraded longitudinally and transversely in each cycle. The WCA and SA were measured after certain cycles.

Acid and alkali resistance

Acid and base solutions, including 98% sulfuric acid and 25% ammonia solution, were adopted to test the acid and base resistance. The as-prepared nanocomposites were soaked in above mentioned solutions for 10 days at room temperature. The pH value of chemical baths was adjusted to be neutral with ammonia and acetic acid after soaking.

Shear stability test

The nanocomposites (1 x 3 cm$^2$) lubricated with three kinds of fluorine free oils were immersed in 100 mL of water in a 100 mL beaker at a stirring speed of 400 rpm for 24 hours. The samples were then dried at 70 °C for 1 h for further measurement. The contact angle hysteresis was measured at different shearing time.

P. aeruginosa biofilm growth and crystal violet (CV) staining

P. aeruginosa colony on a solid Luria−Bertani (LB) agar plate was transferred to 10 mL of a liquid LB culture medium and grown at 37 °C for 12 h. This LB preculture was then seeded at 10% concentration in a liquid LB culture medium in 24-well plate containing representative nanocomposite samples. These bacterial cultures were incubated with shaking at room temperature for 48 hours. Samples were removed from the wells using forceps, gently put on a paper towel to remove excess liquid, and placed in a new 24-well plate. The sample was gently washed 3 times each with 2 mL of normal saline. SEM was used to observe the attached bacteria with and without the above saline washing step. And the following steps were also conducted with and without this washing step to quantify the attached biofilm. Each sample was stained with 1 mL of a CV solution (0.1% CV (w/v) in 95:5 water/ethanol) for 20 min. Excess CV stain was removed by washing twice with 2 mL of deionized water in each individual well, and the sample were thoroughly dried. Then, 0.5 mL of ethanol (95%) was added to the CV-stained samples and incubated with shaking for 2 h. Optical density (OD) measurements of 590 nm of the resulting solutions were taken by a plate reader. Each data point was obtained from three independent samples.

Toxicity screening

Cultures of 1% P. aeruginosa in LB culture medium were grown in duplicate in the presence of 1% (v/v) mineral oil and 1% (w/v) nanocomposite sample. 1% P. aeruginosa in LB culture medium was cultured as control sample. All samples were incubated in an orbital shaker at 37 °C at 250 rpm. OD$_{600}$ was measured by Eppendorf BioPhotometer 6131 Spectrophotometer.

Conflicts of interest

There are no conflicts to declare.
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Notes and references

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