

Research



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Durable superoleophobic polypropylene surfaces

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Polypropylene (PP) is a popular plastic material used in consumer packaging. It would be desirable if such plastic containers were liquid repellent and not so easily fouled by their contents. Existing examples of superoleophobic surfaces typically rely on poorly adhered coatings or delicate surface structures, resulting in poor mechanical durability. Here, we report a facile method for creating superoleophobic PP surfaces via incorporation of nanoparticles (NPs) into the polymer surface. A solvent-NP-PP mixture was spin coated at high temperature to achieve the necessary roughness. Such surfaces were further functionalized with fluorosilane to result in a durable, super-repellent surface. They were also found to exhibit some repellency towards shampoos. This method of incorporating NPs into polymer surfaces could also prove useful in improving the anti-bacterial, mechanical and liquid-repellent properties of plastic devices.

This article is part of the themed issue 'Bioinspired hierarchically structured surfaces for green science'.

1. Introduction

Oil repellency (superoleophobicity) is a desirable surface property for a range of different applications [1] including anti-fouling [2,3], self-cleaning [4], anti-smudge [5,6] and lab-on-chip [7] applications. However, oil repellency is difficult to accomplish as the surface tensions of oils are much lower than that of water, meaning oil droplets are more likely to display contact angles of less than 90° on flat surfaces.

However, high droplet contact angles can still be achieved, even if the contact angle on the flat surface (θ_{flat}) is low, through the use of re-entrant geometries, where surface asperities create an overhang (i.e. become

narrower closer to the surface) [8,9]. This is most commonly achieved through the use of nanoparticles (NPs). To repel liquids with low surface tensions, a low surface energy material is also typically required [10,11]. Fluorinated materials are commonly used as fluorine is very electronegative and has a low polarizability. This results in a low susceptibility to London dispersion forces, leading to weak intermolecular forces, weak cohesive and adhesive forces and therefore low surface energies.

Many existing methods for creating superoleophobic surfaces rely on applying coatings to a substrate and incorporate the necessary roughness and low surface energy material [5,6]. Several use a 'one-pot' technique with all materials mixed and deposited together [12,13]. However, the coatings resulting from these techniques typically suffer from poor durability due to the weak interfacial adhesion between the substrate and the low surface tension material required for oil repellency. Instead of using a coating, it can be desirable to treat the surface of the substrate directly to add roughness and lower the surface tension. Techniques specific to different substrates therefore need to be developed. For example, acid etching has been shown to be an effective way of creating superoleophobic aluminium surfaces [14] and an acetone–NP mixture can result in solvent-induced phase transformation for polycarbonate to create superoleophobic nanocomposite surfaces [15].

Polypropylene (PP) is a common polymer used in a wide variety of applications including consumer packaging, automotive parts and textiles. Water- and oil-repellent PP surfaces are therefore of interest for a wide range of industrial and consumer applications such as in packaging, where it is desirable for the product to be repelled from and not foul the container, reducing wastage and improving the customer experience. PP is commonly found in the bottles and caps used for shampoos, laundry detergents and soaps. Such products contain surfactants, which lower the surface tension of the liquid to aid in cleaning. Surfactant molecules can attach to the walls of the packaging, where they strongly adhere. It would therefore be beneficial if the PP surface could be treated so as to be repellent to water, oils and low surface tension materials. Water repellent PP has been previously demonstrated by solvent casting a PP film from a mixture of good (xylene) and bad (methyl ethyl ketone) solvents (which dissolve and precipitate the polymer respectively) [16] or by dipping the substrate in a xylene–NP solution [17]. In both cases, the samples were found to be superhydrophobic; however, durability experiments were not carried out. In addition, a PP surface that is repellent to water and oils has yet to be created.

In this paper, durable superoleophobic PP has been created through the incorporation of NPs into the polymer surface. The durability and functionality of the surfaces have been tested; durability is important if these surfaces are to be feasible for application in various industries including medical, transportation, construction and consumer goods packaging. Finally, as the NPs are only incorporated near the interface, this technique could be advantageous compared with other polymer nanocomposite fabrication techniques where NPs are distributed throughout the polymer, affecting the properties of the bulk material.

2. Experimental details

In order to achieve structures amenable to creating a superoleophobic surface, the surfaces described in this paper comprise PP treated with a xylene–NP–PP mixture heated to 135°C, figure 1. It is found that spin coating this mixture onto a PP substrate resulted in a nanocomposite polymer surface. By creating polymer–NP composite surfaces in this way, re-entrant geometries suitable for oil repellency are achieved. NPs incorporated deeper into the polymer would have a less pronounced effect on the surface topography. Small, hydrophilic SiO₂ NPs were used as these have been shown to be susceptible to irreversible aggregation, resulting in non-spherical, micrometre-sized clusters [18]. In addition, SiO₂ NPs are known to have high hardness [19], which will aid in the creation of a mechanically durable coating [20]. To achieve the oil repellency, the polymer–NP composite surface was then activated using UV irradiation and treated with

tribometer wear experiment using an optical microscope with a CCD camera (Nikon Optihot-2) to examine any changes [19].

Contact pressures for the tribometer wear experiments were calculated based on Hertz analysis [20]. The elastic modulus of PP, 1.3 GPa [21], was used as an estimate for the elastic modulus of the composite coating and a Poisson's ratio of 0.42 was used [21]. Owing to the inclusion of SiO₂ NPs, the elastic modulus of final coating is expected to be higher, so an underestimated pressure will be obtained with the selected modulus. An elastic modulus of 390 GPa and Poisson's ratio of 0.23 were used for the sapphire ball used in the macroscale wear experiments [22] and the mean contact pressures were calculated as 8.6 MPa and 14.2 MPa for low and high loads, respectively.

(e) Shampoo repellency

To test the repellency of these surfaces towards consumer products, shampoo (Head and Shoulders, Procter and Gamble Co.) was poured onto the surface and the resulting surface-liquid interaction was photographed.

3. Results and discussion

(a) Wettability of surfaces

Untreated PP (flat PP) is found to be slightly hydrophobic with water contact angles of $96 \pm 1^\circ$, table 1 and figure 2. After treatment with the xylene-NP-PP mixture followed by drying in air, the surface became superhydrophobic, with water contact angles of $161 \pm 2^\circ$ and tilt angles of $2 \pm 1^\circ$. This superhydrophobicity is due to inclusion of NPs in the xylene mixture leading to the formation of a rough surface. The PP dissolved in the xylene helps to bind the NPs to the substrate after spin coating. The resulting rough surface contains a hierarchical surface morphology with re-entrant, overhanging geometry, figure 3. This morphology is sufficient to create a superhydrophobic state in water due to the ability of the hierarchical surface to trap air and thus create a composite interface. However, owing to the low contact angles for hexadecane on flat PP ($35 \pm 2^\circ$), the xylene-treated surface is superoleophilic with hexadecane fully wetting the surface, figure 2. To attain superoleophobicity, a low surface energy material is also required.

After UV activation (to facilitate silane attachment) and fluorosilane treatment, the surface becomes superhydrophobic and superoleophobic with contact angles of $172 \pm 1^\circ$ and $159 \pm 1^\circ$ for water and hexadecane, respectively, figure 2. The combination of the fluorosilane with the re-entrant, hierarchical structures obtained from NP incorporation enables the formation of a favourable liquid-vapour interface for lower surface tension liquids, such as hexadecane, that exhibit contact angles less than 90° on the corresponding flat surface.

In order to optimize the surface, the concentration of NPs in the xylene solvent was varied. The hexadecane tilt angle was used as a measure of optimizing the surface treatment, figure 4. An optimum hexadecane tilt angle of $4 \pm 1^\circ$ was found on the fluorinated PP-NP composite surface resulting from a xylene-NP mixture concentration of around 8–9 mg ml⁻¹. Above this concentration and the hexadecane tilt angle begins to rise due to contact line pinning on the surface features.

(b) Wear resistance of surface

The mechanical durability of the polymer-NP composite surface was investigated through the use of tribometer wear experiments and the resulting optical images, showing a portion of the wear track, are displayed in figure 5. The initial wear experiments were carried out with a load of 10 mN; however, no observable defect was found on the surface after this experiment and the surface remained oil repellent, suggesting good fluorosilane attachment to the polymer. Therefore, to further test the durability of the surface, the load was increased to 45 mN. This

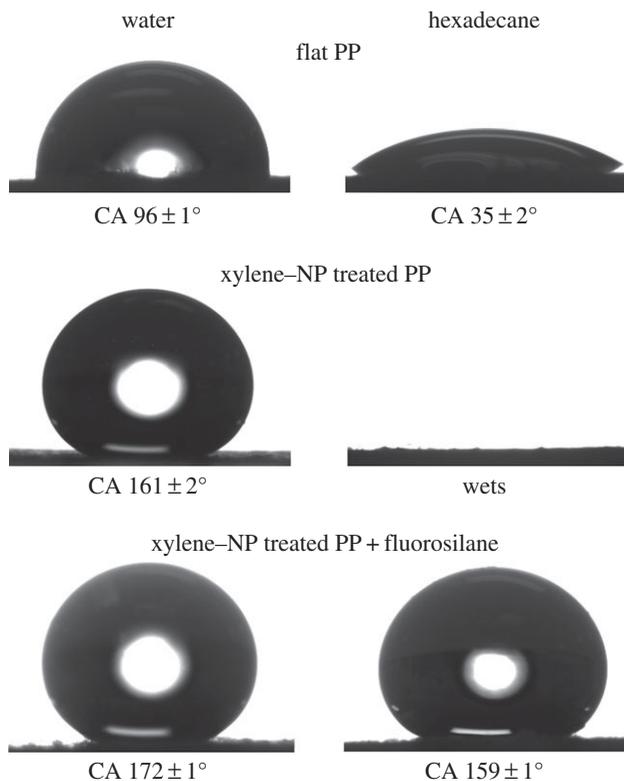


Figure 2. Contact angle (CA) images for droplets of water and hexadecane on: flat PP, PP–NP composite surfaces and fluorinated PP–NP composite surfaces.

Table 1. Comparison of static contact angles and tilt angles for water and hexadecane droplets deposited on polypropylene (PP) surfaces.

surface	water		hexadecane	
	contact angle (°)	tilt angle (°)	contact angle (°)	tilt angle (°)
flat PP	96 ± 1	n.a.	35 ± 2	n.a.
flat PP + fluorosilane	110 ± 2	n.a.	76 ± 2	n.a.
PP–NP composite surface	161 ± 2	2 ± 1	approximately 0	n.a.
PP–NP composite surface + fluorosilane	172 ± 1	1 ± 1	159 ± 1	4 ± 1

increased load resulted in an observable wear scar, upon which hexadecane droplets were found to pin (tilt angle increases) when rolled over the wear scar location. However, the images confirmed that the surface features were not completely destroyed and the surface may regain its oleophobicity after re-application of the fluorosilane layer. It is believed that these surfaces are significantly more durable than many other examples of superoleophobic surfaces, which typically rely on poorly adhered coatings or delicate surface structures. Many studies typically report either poor mechanical properties or fail to report any durability data.

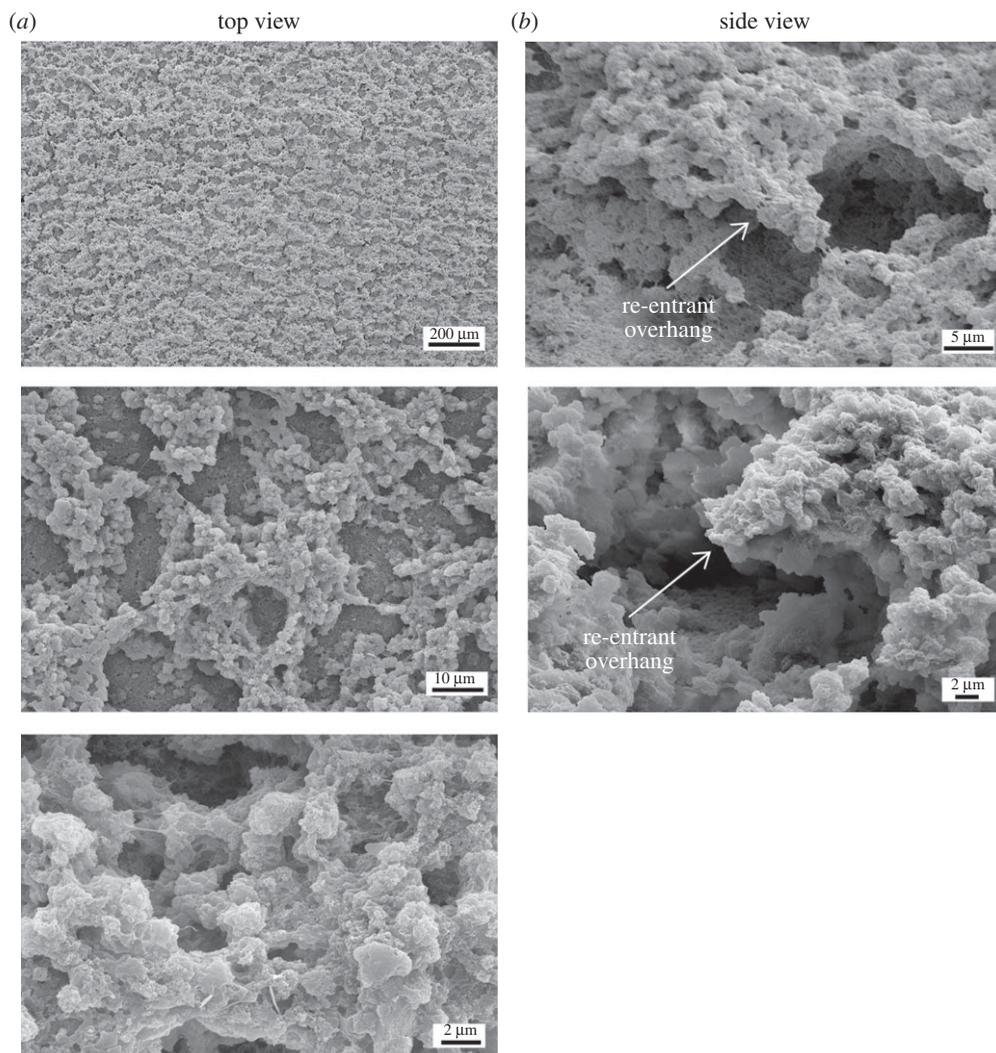


Figure 3. SEM images of superoleophobic PP after spin coating of an optimized xylene–NP–PP mixture. (a) Top view and (b) side view showing re-entrant, overhang geometry (sample tilted 70°).

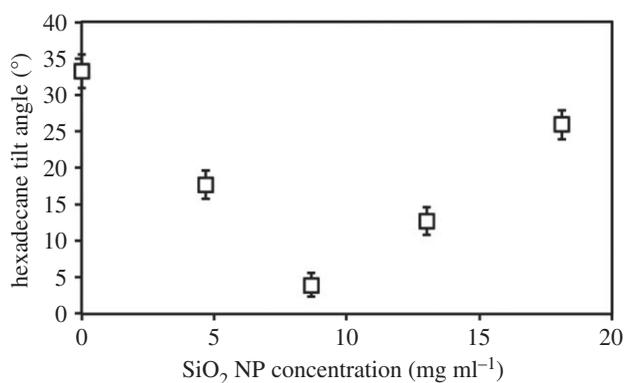


Figure 4. Graph to show hexadecane tilt angles on fluorinated PP–NP composite surfaces as a function of SiO₂ NP concentration used during xylene–NP–PP treatment.

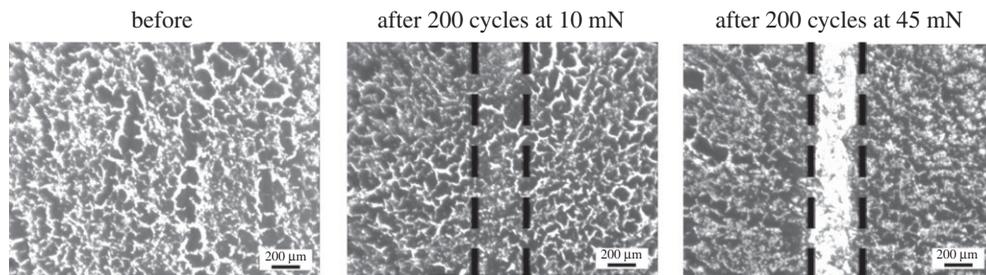


Figure 5. Optical micrographs before and after wear experiments using ball-on-flat tribometer using a 3 mm diameter sapphire ball at 10 mN and 45 mN loadings for fluorinated PP–NP composite surfaces.

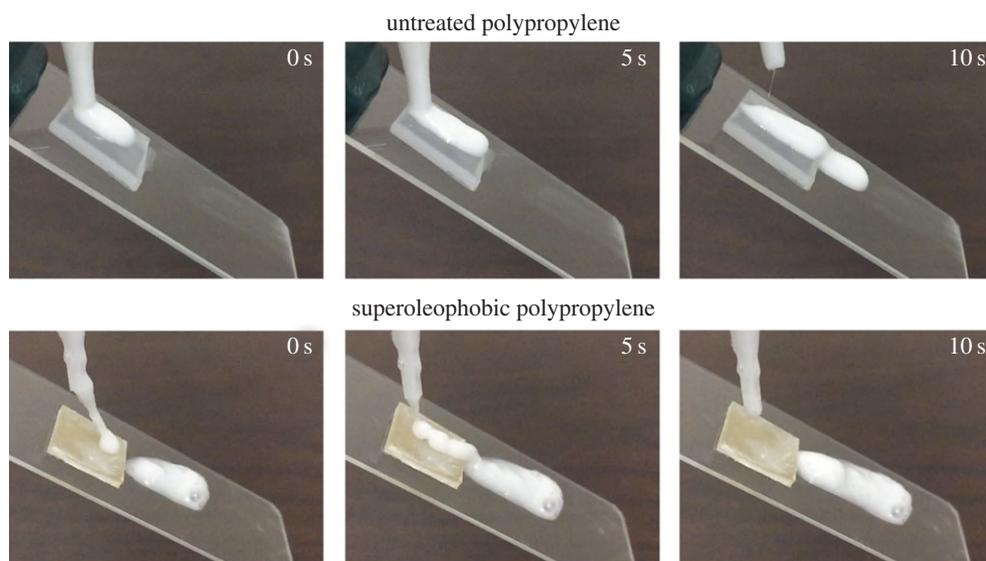


Figure 6. Photographs demonstrating shampoo repellency of superoleophobic PP compared to an untreated sample. (Online version in colour.)

(c) Shampoo repellency

PP is a common material used in the creation of bottles and bottle caps for consumer products. One such product is shampoos, which comprise surfactants among other ingredients. To test the surface repellency towards these liquids, shampoo was poured over the superoleophobic PP. During testing, it was found that the superoleophobic PP surface was able to repel the shampoo, with the viscous liquid sliding down the surface with no visible product remaining on the substrate, as seen in figure 6. This is compared to shampoo deposited onto untreated PP, which remains for a greater period of time and fouls the surface. However, if shampoo is left on the superoleophobic PP surface for a significant amount of time, there is some reduction in the repellent nature of the material. The superoleophobic material reported here could therefore find use in applications where contact with the fouling product is minimal (such as bottle cap or single-use applications). However, more work is required to fully achieve shampoo repellency for PP surfaces in constant contact with shampoo such as the inside of a typical consumer bottle.

4. Conclusion

Durable superoleophobic PP surfaces have been created through a facile method involving the spin coating of a xylene–NP–PP mixture. Following UV activation and fluorosilane coupling,

the low surface energy material, combined with the re-entrant surface structures, results in a surface that displays both high contact angles and low tilt angles for water and hexadecane. The super-repellent surfaces were found to be more durable compared with existing superoleophobic surfaces and coatings. The surfaces were also found to repel shampoo to some extent, with droplets sliding from the surface. However, long-term repellency to shampoo remains a challenge. Such incorporation of NPs into existing polymer surfaces is an attractive way to improve the anti-bacterial, mechanical and liquid-repellent properties of plastic devices.

Authors' contributions. P.S.B. performed the experiments and analysed the data. P.S.B. wrote the main text and P.S.B. and B.B. participated equally in planning, execution and review of the manuscript.

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References

1. Bhushan B. 2016 *Biomimetics: bioinspired hierarchical-structured surfaces for green science and technology*, 2nd edn. Cham, Switzerland: Springer International.
2. Bixler GD, Bhushan B. 2012 Biofouling: lessons from nature. *Phil. Trans. R. Soc. A* **370**, 2381–2417. (doi:10.1098/rsta.2011.0502)
3. Zhu X, Loo H-E, Bai R. 2013 A novel membrane showing both hydrophilic and oleophobic surface properties and its non-fouling performances for potential water treatment applications. *J. Membr. Sci.* **436**, 47–56. (doi:10.1016/j.memsci.2013.02.019)
4. Nishimoto S, Bhushan B. 2013 Bioinspired self-cleaning surfaces with superhydrophobicity, superoleophobicity, and superhydrophilicity. *RSC Adv.* **3**, 671–690. (doi:10.1039/C2RA21260A)
5. Brown PS, Bhushan B. 2015 Mechanically durable, superoleophobic coatings prepared by layer-by-layer technique for anti-smudge and oil-water separation. *Sci. Rep.* **5**, 8701. (doi:10.1038/srep08701)
6. Brown PS, Bhushan B. 2015 Bioinspired, roughness-induced, water and oil super-phobic and super-phobic coatings prepared by adaptable layer-by-layer technique. *Sci. Rep.* **5**, 14030. (doi:10.1038/srep14030)
7. Gogolides E, Ellinas K, Tserepi A. 2015 Hierarchical micro and nano structured, hydrophilic, superhydrophobic and superoleophobic surfaces incorporated in microfluidics, microarrays and lab on chip microsystems. *Microelectron. Eng.* **132**, 135–155. (doi:10.1016/j.mee.2014.10.002)
8. Brown PS, Bhushan B. 2016 Designing bioinspired superoleophobic surfaces. *APL Mater.* **4**, 015703. (doi:10.1063/1.4935126)
9. Nosonovsky M, Bhushan B. 2008 *Multiscale dissipative mechanisms and hierarchical surfaces*. Heidelberg, Germany: Springer.
10. Kumar RTR, Mogensen KB, Bøggild P. 2010 Simple approach to superamphiphobic overhanging silicon nanostructures. *J. Phys. Chem. C* **114**, 2936–2940. (doi:10.1021/jp9066422)
11. Tuteja A, Choi W, Mabry JM, McKinley GH, Cohen R. 2008 Robust omniphobic surfaces. *Proc. Natl Acad. Sci. USA* **105**, 18 200–18 205. (doi:10.1073/pnas.0804872105)
12. Hsieh C-T, Chen J-M, Kuo R-R, Lin T-S, Wu C-F. 2005 Influence of surface roughness on water- and oil-repellent surfaces coated with nanoparticles. *Appl. Surf. Sci.* **240**, 318–326. (doi:10.1016/j.apsusc.2004.07.016)
13. Muthiah P, Bhushan B, Yun K, Kondo H. 2013 Dual-layered-coated mechanically-durable superomniphobic surfaces with anti-smudge properties. *J. Colloid Interface Sci.* **409**, 227–236. (doi:10.1016/j.jcis.2013.07.032)
14. Peng S, Bhushan B. 2015 Mechanically durable superoleophobic aluminum surfaces with microstep and nanoreticula hierarchical structure for self-cleaning and anti-smudge properties. *J. Colloid Interface Sci.* **461**, 273–284. (doi:10.1016/j.jcis.2015.09.027)
15. Brown PS, Bhushan B. 2016 Durable, superoleophobic polymer–nanoparticle composite surfaces with re-entrant geometry via solvent-induced phase transformation. *Sci. Rep.* **6**, 21048. (doi:10.1038/srep21048)
16. Erbil HY, Demirel AL, Avci Y, Mert O. 2003 Transformation of a simple plastic into a superhydrophobic surface. *Science* **299**, 1377–1380. (doi:10.1126/science.1078365)

17. Contreras CB, Chagas G, Strumia MC, Weibel DE. 2014 Permanent superhydrophobic polypropylene nanocomposite coatings by a simple one-step dipping process. *Appl. Surf. Sci.* **307**, 234–240. (doi:10.1016/j.apsusc.2014.04.019)
18. Pham KN, Fullston D, Sagoe-Crentsil K. 2007 Surface charge modification of nano-sized silica colloid. *Aust. J. Chem.* **60**, 662–666. (doi:10.1071/CH07138)
19. Ebert D, Bhushan B. 2012 Durable Lotus-effect surfaces with hierarchical structure using micro- and nanosized hydrophobic silica particles. *J. Colloid Interface Sci.* **368**, 584–591. (doi:10.1016/j.jcis.2011.09.049)
20. Bhushan B. 2013 *Introduction to tribology*, 2nd edn. New York, NY: Wiley.
21. Anonymous. 2014 Typical engineering properties of polypropylene. See <http://www.ineos.com/globalassets/ineos-group/businesses/ineos-olefins-and-polymers-usa/products/technical-information-patents/ineos-engineering-properties-of-pp.pdf> (accessed 12 May 2016).
22. Bhushan B, Gupta BK. 1991 *Handbook of tribology: materials, coatings, and surface treatments*. New York, NY: McGraw-Hill.