Journal of Thermal Science and Technology
Vol. 6, No. 2, 2011

Superhydrophobicity of Self-Organized Surfaces of Polymer Nanowire Arrays Fabricated by a Nano-Injection Moulding Technique*

Bing-Yang CAO**, Yuan-Wei LI**, Ruo-Yu DONG**, Jie KONG***,
Heng CHEN***, Yan XU**** and Kai-Leung YUNG****
** Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China
E-mail: caoby@tsinghua.edu.cn
*** Department of Applied Chemistry, School of Science, Northwestern Polytechnical University
Xi'an 710072, P. R. China
**** Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong, P. R. China

Abstract

We report on the superhydrophobicity of self-organized surfaces of polyethylene (PE) nanowire arrays that are fabricated by a nano-injection moulding technique. The highly-aligned PE nanofibers with high aspect ratio are formed after the infiltration of polymer melts into the alumina nanopores by wetting action and fluid vibrational perturbation. The self-organized surfaces of polymer nanowire arrays are found to have micro-to-nanoscale hierarchical nanostructures, and have superhydrophobicity of >150° contact angles. The present superhydrophobic surfaces may be quite promising due to its simple but massive production with high quality.

Key words: Superhydrophobicity, Contact Angle, Nanostructure Surface, Nanowire Array, Nano-Injection Moulding Technique

1. Introduction

Superhydrophobic surfaces are highly desired in the fields of micro-/nanoscale heat transfer and fluid flow. As for the heat transfer, the small tension of a superhydrophobic surface may greatly decrease the interaction between a liquid droplet and the solid so that the superhydrophobic surface can supply anti-icing or anti-dewing properties,(1-3) control the solid-liquid thermal resistance,(4-6) and produce very high boiling heat transfer coefficient (7). In addition, liquid flow and droplet control in micro- and nanochannels are widely used in recently advanced MEMS/NEMS and biochip systems.(8-10) Surface effects substantially dominate the fluid flow due to the high surface-to-volume ratio in such micro- and nanoscale devices. Recently quite a few literatures have been published to show that liquids flowing over a solid surface do slip and the no-slip boundary condition is merely an approximation at macroscopic scale. The velocity slip of liquid flows at a solid surface has been measured experimentally and simulated by molecular dynamics simulations as reviewed in Ref. 10. Wettability of a surface is shown to be one of the dominant factors. A hydrophobic surface can effectively enhance the velocity slip, and consequently decrease the flow friction.(10-14)

*Received 31 Jan., 2011 (No. 11-0079)
[DOI: 10.1299/jtst.6.204]

Originally inspired by the unique property of superhydrophobicity of lotus leaves(15) and water strider legs(16), which is specially called the "Lotus Effect", researchers try to produce superhydrophobic surfaces through nanostructuring them. Traditional ways mainly include creating rough structures on a hydrophobic surface and modifying a rough surface by materials with low surface free energy. Various processes have been developed to fabricate micro/nano-patterns with superhydrophobicity based on silicon, metal, glass, carbon nanotubes, polymer, or organic coatings.(17,18) Among these technologies, the micro/nano-injection moulding method has advantages of simple fabrication, high-quality, low-cost, mass-production, (19,20) especially for micro-/nanoscale fluidic and heat transfer devices.

In this paper, we report on the fabrication of superhydrophobic self-organized surfaces of high-density polyethylene (HDPE) nanowire arrays by a nano-injection moulding method. The surface shows superhydrophobicity and its contact angle reaches >150°, which is attributed to the self-organized and hierarchical surface nanostructures. Theoretical analyses based on the Cassie model are also presented.

2. Fabrication of Nanowire Arrays

The nanoporous template wetting technique, originally developed by Steinhart et al. (21), is now improved to enhance the polymer infiltration into the nanopores by a high-frequency fluid pulsation strategy, as schematically shown in Fig. 1. Actually, the main part of the setup is a chamber with the pressure controlled by the pressure meter, the temperature controlled by the thermal cycle spring, and the vibrational perturbation generated by the piezoelectric transducer and amplifier. In the original nanoporous template wetting technique, the polymer infiltration is driven by the capillary force. In the present nano-injection moulding technique, the polymer injection process is mainly driven by the resultant action of the capillary force, pressure and vibrational perturbation. During the infiltration process, a vibration with a frequency about ~10 KHz induced by the piezoelectric transducer is imposed. This technique is able to produce several times longer polymer nanowires compared with the original wetting template technique.(22) It indicates that the present injection is dominated by vibrational hydrodynamics rather than just by wetting behaviors.

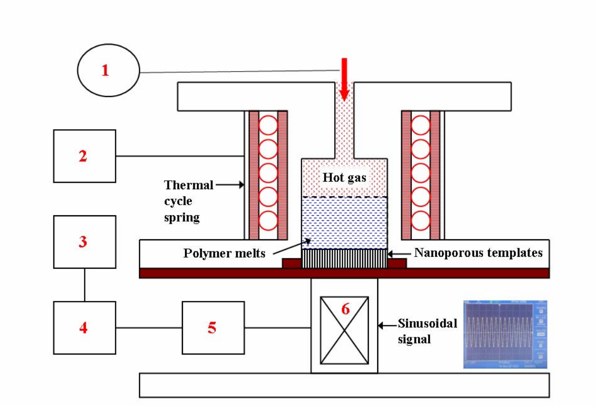

Figure 1 Schematic of the fabrication system by the nano-injection moulding technique. (1) Pressure meter; (2) Temperature controller; (3) Oscilloscope; (4) Alternating current generator; (5) Piezoelectric amplifier; (6) Piezoelectric transducer.

The fabrication procedure is schematically shown in Fig. 2. First, the porous anodic alumina (PAA) templates with pore diameters of 200 nm are purchased from Whatman, Inc. The PAA templates are freestanding disks with a diameter of 13 mm, and their pores are all through-hole. The PAA templates are firstly treated with solvents of different polarities, i.e. ethanol, acetone, chloroform and hexane in sequence. Second, the HDPE films with thickness of about 300 μm, density of 0.945 g/cm^3 and melting index of 13.0 g/10 min are obtained from Qilu Petroleum and Chemical Co. of China. A HDPE film is then placed on the top of a template with a good contact. Third, the sample is placed into the chamber, and the chamber containing the PE film and template sample is then heated to 160 ºC by the thermal cycle springs, well above the melting point of HDPE (130 ºC), to excite the infiltration of the PE melts into the nanopores of template. Under the driving from the capillary force, pressure and vibration, the PE melts infiltrate into the nanopores. Actually we can control the infiltration length by adjusting the infiltration time. In the present paper, two hours of infiltration may prepare us nanowire arrays with about 50 μm in thickness. Moreover, the vibration does help the polymer chains to be more oriented due to the oscillatory shear rates(23,24) so that the present polymer nanowire arrays also have very high thermal conductivity (more than 10 W/mK)(25). Fourth, the sample is cooled down to ambient temperature. The polymer melts solidify gradually. Finally, the HDPE nanowire arrays are then released by removing the template in NaOH aqueous solution and being rinsed with deionized water and ethanol and being dry at 30 ºC in vacuum in sequence.

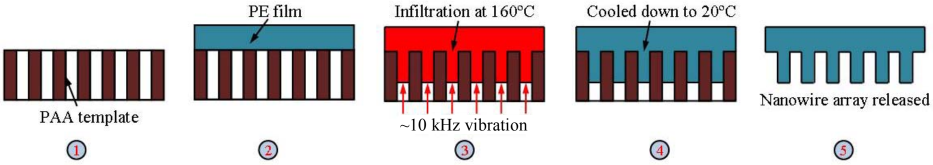

Figure 2　Fabrication procedure of the nano-injection moulding technique. (1) Template; (2) Sample including PE film and template; (3) Infiltration; (4) Solidification; (5) Nanowire array releasing.

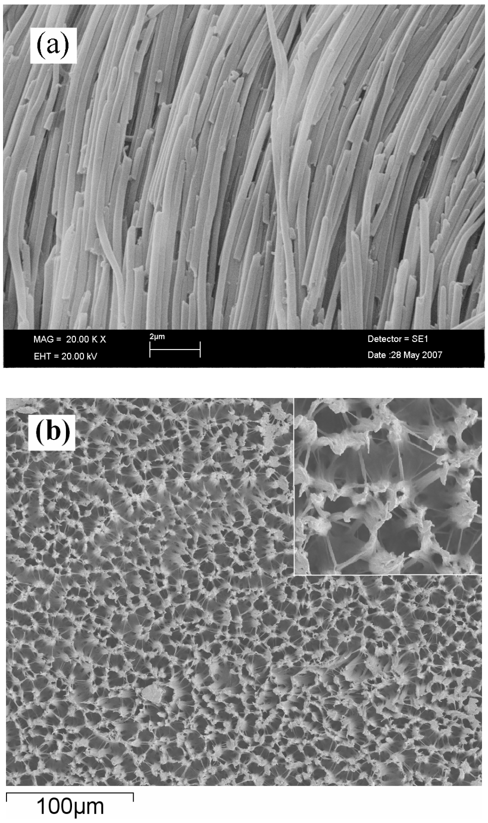

Figure 3　Cross-section (a) and top view (b) SEM images of the HDPE nanowire array surfaces.

3. Results and discussion

The cross-section and top view images, characterized by scanning electron microscopy (SEM, Leica Stereoscan 440) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F), of the as-fabricated HDPE nanowire array are shown in Figs. 3. All samples were coated with 5 nm Au before measurements. From Fig. 3(a), we can see that the nanowires are of high quality, such as well-defined, straight, smooth in surface and uniform in diameter, thanks to the good PAA templates. From the top view SEM images shown in Fig. 3(b), we can see that the nanowire array surface has a micro-to-nanoscale hierarchical structure. During the releasing process of the nanowire arrays, the solvent evaporates and dries gradually, and the nanowires are very easy to form bundles. The construction of the bundles is random in direction and orientation, i.e. self-organized. Therefore, the surface structure spans microscale to nanoscale, and is hierarchical. For the lotus leaf, the micro- and nanoscale hierarchical structures, like fractal topology, on the surface contribute to its superhydrophobicity.(17) A surface with multiscale character was found to be better for its hydrophobicity enhancement.(26) Therefore, the present self-organized hierarchical structures are greatly helpful for enhancing the surface hydrophobicity.

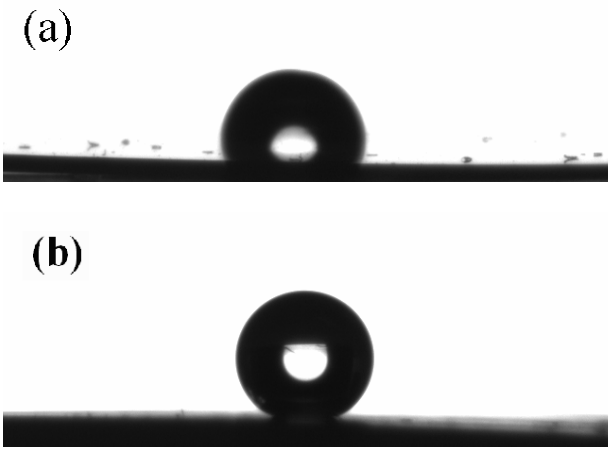

Figure 4 Contact angles of water droplet on native HDPE surface (a), and nanowire array surface (b).

The wettabilities of the flat and self-organized HDPE surfaces are characterized by a high-speed contact angle measuring system (OCAH 200, Dataphysics, Germany) at room temperature (20 ºC). The HDPE native flat surface shows slightly hydrophobic with a water contact angle of about 102.2°, as shown in Fig. 4(a). The reference values from literature [22,27,28] range 99°-104.4°. While the nanowire array surface show much higher hydrophobicity with a water contact angle of about 151.8°, as shown in Fig. 4(b). We can say that the present nano-injection technique, having advantages of simple, massive production and high quality, can prepare us superhydrophobic polymer surfaces. The technique is promising for developing micro-/nanoscale fluidic and heat transfer devices. It should be pointed out that there may be still room for us to optimize the hydrophobicity of the polymer nanowire array surfaces through varying the nanowire diameter, length, releasing parameters etc.

Traditionally, the wettability of a rough surface can be characterized by the well-known Cassie model(29). The interaction between a droplet and a rough surface is weakened by patches of air beneath the micro-to-nanoscale hierarchical nanostructures. The Cassie model for rough surfaces is

$$\theta_n = \cos^{-1}(f\cos\theta_f + f - 1) \tag{1}$$

where θ_n and θ_f are, respectively, the contact angles of the nanowire array and flat surfaces, f is the area fraction of the liquids contacting with the surface. For the present nanowire array surface, we have θ_n=151.8° and θ_f=102.2°, so the area fraction of the present self-organized surface is only 15%.

4. Conclusions

We report on the superhydrophobicity of self-organized surfaces of polyethylene (PE) nanowire arrays that are fabricated by a nano-injection moulding technique. The self-organized surfaces of polymer nanowire arrays are found to have micro-to-nanoscale hierarchical structures, and have superhydrophobicity of >150° contact angles. Based on the Cassie model, the area fraction of the present self-organized surface is only 15%.The present superhydrophobic surfaces may be quite promising for developing micro-/nanoscale fluidic and heat transfer devices due to its simple but massive production with high quality.

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China (No. 50976052, 50730006), Aero-Science Fund of China (No. 2009ZH53073), Chunhui Plan of Ministry of Education of China (Z2009-1-71004), Aoxiang Star Project in Northwestern Polytechnical University, and funding from the Hong Kong Research Grants Council (PolyU 5347/08E).

References

(1) L.L. Cao, A.K. Jones, V.K. Sikka, J.Z. Wu and D. Gao, (2009): “Anti-Icing Superhydrophobic Coatings”, Langmuir, Vol. 25, No. 21, pp. 12444-12448.

(2) S.A. Kulinich and M. Farzaneh, (2009): “How Wetting Hysteresis Influences Ice Adhesion Strength on Superhydrophobic Surefaces”, Langmuir, Vol. 25, No. 16, pp. 8854-8856.

(3) A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley and R.E. Cohen, (2010): “Relationships between Water Wettability and Ice Adhesion”, Applied Materials and Interfaces, Vol. 2, No. 11, pp. 3100-3110.

(4) Z.B. Ge, D.G. Cahill and P.V. Braun, (2006): “Thermal Conductance of Hydrophilic and Hydrophobic Interfaces”, Physical Review Letters, Vol. 96, pp. 186101.

(5) B.H. Kim, A. Beskok and T. Cagin, (2008): “Molecular Dynamics Simulations of Thermal Resistance at the Liquid-Solid Interface”, Journal of Chemical Physics, Vol. 129, pp. 174701.

(6) M. Shibahara and K. Takeuchi, (2011): “A Molecular Dynamics Study on the Effects of Nanostructural Clearances on Thermal Resistance at a Lennard-Jones Liquid-Solid Interface”, Journal of Thermal Science and Technology, Vol. 6, No. 1, pp. 9-20.

(7) R,K. Chen, M.C. Lu, V. Srinivasan, Z.J. Wang, H.H. Cho and A. Majumdar, (2009): “Nanowires for Enhanced Boiling Heat Transfer”, Nano Letters, Vol. 9, No. 2, pp. 548-553.

(8) C.M. Ho and Y.C. Tai, (1998): “Micro-Electro-Mechanical-Systems (MEMS) and Fluid Flows”, Annual Review of Fluid Mechanics, Vol. 30, pp. 597-612.

(9) H.G. Craighead, (2000): “Nanoelectromechanical Systems” Science, Vol. 290, pp. 1532-1535.

(10) B.Y. Cao, J. Sun, M. Chen and Z.Y. Guo, (2009): “Molecular Momentum Transport at Fluid-Solid Interfaces in MEMS/NEMS”, International Journal of Molecular Sciences, Vol. 10, pp. 4638-4706.

(11) J.L. Barrate and L. Bocquet, (1999): “Large Slip Effect at a Nonwetting Fluid-Solid Interface”, Physical Review Letters, Vol. 82, No. 23, pp. 4671-4674.

(12) B.Y. Cao, M. Chen and Z.Y. Guo, (2006): "Liquid Flow in Surface-Nanostructured Channels Studies by Molecular Dynamics Simulation", Physical Review E, Vol. 74, pp. 066311.

(13) C. Ybert, C. Barentin, C. Cottin-Bizonne, P. Joseph and L. Bocquet, (2007): "Achieving Large Slip with Superhydrophobic Surfaces: Scaling Laws for Generic Geometries", Physics of Fluids, Vol. 19, pp. 123601.

(14) A. Martini, A. Roxin, R.Q. Snurr, Q. Wang and S. Lichter, (2008): "Molecular Mechanisms of Liquid Slip", Journal of Fluid Mechanics, Vol. 600, pp. 257-269.

(15) W. Barthlott and C. Neinhuis, (1997): "Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces", Planta, Vol. 202, pp. 1-8.

(16) X.F. Gao and L. Jiang, (2004): "Water-Repellent Legs of Water Striders", Nature, Vol. 432, pp. 36.

(17) L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, J. Zhai, Y.L. Song, B.Q. Liu, L. Jiang and D.B. Zhu, (2002): "Super-Hydrophobic Surfaces: From Natural to Artificial", Advanced Materials, Vol. 14, pp. 1857-1860.

(18) X.J. Feng and L. Jiang, (2006): "Design and Creation of Superwetting/Antiwetting Surfaces", Advanced Materials, Vol. 18, pp. 3063-3078.

(19) U.M. Attia, S. Marson and J.R. Alcock, (2009): "Micro-Injection Moulding of Polymer Microfluidic Devices", Microfluidics and Nanofluidics, Vol. 7, pp. 1-28.

(20) S.H. Kim, J.H. Jeong and J.R. Youn, (2010): "Nanopattern Insert Molding", Nanotechnology, Vol. 21, pp. 205302.

(21) M. Steinhart, J.H. Wendorff, A. Greiner, R.B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi and U. Gosele, (2002): "Polymer Nanotubes by Wetting of Ordered Porous Templates", Science, Vol. 296, pp. 1997.

(22) J. Kong, Y. Xu, K.L. Yung, Y.C. Xie and L. He, (2009): "Enhanced Polymer Melts Flow through Nanoscale Channels under Vibration", Journal of Physical Chemistry C, Vol. 113, pp. 624-629.

(23) S. Rendon, W.R. Burghardt, M.L. Auad and J.A. Kornfield, (2007): "Shear-Induced Alignment of Smectic Side Group Liquid Crystalline Polymers", Macromolecules, Vol. 40, pp. 6624-6630.

(24) M.C. Garcia-Gutierrez, A. Linares, J.J. Hernandez, D.R. Rueda, T.A. Ezquerra, P. Poza and R.J. Davies, (2010): "Confinement-Induced One-Dimensional Ferroelectric Polymer Arrays", Nano Letters, Vol. 10, pp. 1472-1476.

(25) B.Y. Cao, Y.W. Li, J. Kong, H. Chen, Y. Xu, K.L. Yung and A. Cai, (2011): "High Thermal Conductivity of Polyethylene Nanowire Arrays Fabricated by an Improved Nanoporous Template Wetting Technique", Polymer, Vol. 52, pp. 1711-1715.

(26) A.W. Adamson and A.P. Gast, (1997): "Physical Chemistry of Surfaces", Wiley: New York.

(27) E. Puukilainen, H.K. Koponen, Z.L. Xiao, S. Suvanto and T.A. Pakkanen, (2006): "Nanostructured and Chemically Modified Hydrophobic Polyolefin Surfaces", Colloids and Surfaces A, Vol. 287, pp. 175-181.

(28) C.W. Extrand, (2003): "A Thermodynamic Model for Wetting Free Energies from Contact Angles", Langmuir, Vol. 19, pp. 646-649.

(29) A.B.D. Cassie and S. Baxter, (1944): "Wettability of porous surfaces", Transactions of the Faraday Society, Vol. 40, pp. 546-551.