Preparation and characterization of self-cleaning stable superhydrophobic linear low-density polyethylene

Zhiqing Yuan\textsuperscript{1,3}, Hong Chen\textsuperscript{2}, Jide Zhang\textsuperscript{1}, Dejian Zhao\textsuperscript{1}, Yuejun Liu\textsuperscript{1}, Xiaoyuan Zhou\textsuperscript{1}, Song Li\textsuperscript{1}, Pu Shi\textsuperscript{1,3}, Jianxin Tang\textsuperscript{1} and Xin Chen\textsuperscript{1}

\textsuperscript{1} School of Packaging and Printing, Hunan University of Technology, Zhuzhou, Hunan 412008, People’s Republic of China
\textsuperscript{2} Central South University of Forestry and Technology, Changsha, Hunan 410004, People’s Republic of China
\textsuperscript{3} State Key laboratory for Powder Metallurgy, Central South University Changsha, Hunan 410083, People’s Republic of China

E-mail: byxy2001@163.com and chenhongcs@126.com

Received 10 March 2008
Accepted for publication 3 October 2008
Published 10 December 2008
Online at stacks.iop.org/STAM/9/045007

Abstract
Porous superhydrophobic linear low-density polyethylene (LLDPE) surface was prepared by a simple method. Its water contact angle and sliding angle were 153±2° and 10°, respectively. After contamination, 99% of the contaminant particles were removed from the superhydrophobic LLDPE surface using artificial rain. The superhydrophobic LLDPE surface showed high stability in the pH range from 2 to 13. When LLDPE samples were stored in ambient environment for one month, their water contact angle and sliding angle remained constant. Their superhydrophobic property was also maintained after annealing in the temperature range 10–90°C.

Keywords: superhydrophobic, linear low-density polythene, self-cleaning, contact angle, sliding angle

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

1. Introduction
For a solid surface, wettability is an important property governed by both the chemical composition and geometrical structures of solid surfaces [1]. A surface with a water contact angle greater than 150° is commonly called superhydrophobic [2]. In nature, there are many natural superhydrophobic species such as sacred lotus leaves [3], taro leaves [4], and water strider’s legs [5]. These surfaces are water-repellent in that droplets roll off them at a small tilt angle (sliding angle), thereby removing contaminants from the surface [6] and thus showing a self-cleaning property. Because of their self-cleaning property and limited contact area between solid surfaces and water, superhydrophobic surfaces have great potential applications in both industrial and agriculture fields [7]. Recently, the preparation of artificial superhydrophobic surfaces has attracted much attention, and many methods of fabricating superhydrophobic surfaces, such as the solution method [8], sol–gel method [9–12], plasma fluorination method [13–17], electrospinning method [18–25], template method [26–29], layer-by-layer self-assembly [30–34], and other methods [35–43] have been proposed. However, most of these methods are rather complicated. Therefore, developing a facile and inexpensive approach to obtaining a stable superhydrophobic surface is important. In this study, we prepared a superhydrophobic linear low-density polyethylene (LLDPE) using a simple method, and studied LLDPE self-cleaning property, wettability and stability. Superhydrophobic low-density polyethylene (LDPE) has already been reported [16, 44];
Figure 1. SEM images of LLDPE surfaces obtained by drying pure LLDPE solutions at different temperatures: (a) 120 °C, (b) 5 °C, (c) shows a SEM image of the as-prepared superhydrophobic LLDPE surface obtained by adding 10 ml of ethanol to the LLDPE solution. Inset images show water contact angles.

however, to the best of our knowledge, there are at present only a few papers that describe superhydrophobic LLDPE. LLDPE has the same chemical composition as LDPE, but its molecular chain structures and crystallization degree differ from those of LDPE, and many physical properties of LLDPE are better than those of LDPE. Hence, LLDPE has wider applications in both agricultural and industrial fields.

2. Experimental details

2.1. Materials

Commercial-grade LLDPE (Maoming Petroleum Chemical Corporation of China, density $d = 0.91$ g cm$^{-3}$) was used without any further treatment. Xylene (mixture of isomers, obtained from Changsha Huihong Chemical Plant of China) was chosen as the solvent. Glass plates were cleaned with detergent, rinsed in deionized water several times, and dried in nitrogen gas.

2.2. Preparation of superhydrophobic LLDPE surface

First, 0.1 g of LLDPE resin was dissolved slowly in 10 ml of xylene to form a solution at 120 °C. Then, 10 ml of ethanol was added to the LLDPE solution. After stirring for 2 min, the solution was cast onto the cleaned glass plates. After drying for 10 h in ambient atmosphere (relative humidity 50%), a porous superhydrophobic LLDPE surface was obtained.

2.3. Characterization

The wettability of the LLDPE surfaces was measured on a DataPhysics OCA 20 contact-angle system at ambient temperature using 5 µl droplets. Sliding angle was measured by tilting the sample stage from 0° to higher angles and then placing a droplet on the sample using a micro-gauge. When the droplet rolled off the surface, the angle of the sample stage was the sliding angle. The surface morphologies of the LLDPE surfaces were observed by scanning electron microscopy (SEM, HITACHI S-3000N).

3. Results and discussion

When a pure LLDPE solution was cast onto the substrates and dried at 120 °C, a smooth LLDPE surface was obtained, and the water contact angle was only 102 ± 1.8° (figure 1(a)). To increase the water contact angle of the LLDPE surface, the surface roughness should be enhanced according to the Wenzel model [45]. For the polymer solution, decreasing the drying temperature generally caused phase separation, and a rough surface was obtained [8, 44]. Thus, we dried
the pure LLDPE solution at ambient temperature (within 5–10°C). The resulting surface (shown in figure 1(b)) was rougher than the smooth LLDPE surface, and the water contact angle increased to 127 ± 2.1°. However, it was still far from achieving superhydrophobicity (150°), indicating that decreasing drying temperature alone is not sufficient for obtaining a superhydrophobic LLDPE surface. To obtain such surface, surface roughness should be further increased, and the preparation process should be modified. Adding appropriate non-solvents to polymer solutions helps to obtain a superhydrophobic surface [8]. Note that ethanol does not dissolve LLDPE. Thus, we added 10 ml of ethanol to the LLDPE solution to modify the preparation process. Interestingly, a porous and rougher LLDPE surface was obtained (shown in figure 1(c)); the average diameter of the pores is about 2 µm, and air can be trapped in these pores. Thus, the porous LLDPE surface can be considered as a composite comprising air trapped in the pores and a nanorod-like LLDPE. Cassie and Baxter [46] proposed
cosθ = f1 cosθ − f2
(1)
to describe the contact angle θ of a hydrophobic surface comprised of solid and air. Here, f1 and f2 are the fractions of the solid surface and air in the composite surface, respectively (i.e. f1 + f2 = 1), whereas θ is the equilibrium contact angle on a flat solid surface. This equation predicts that increasing the fraction of air (f2) would increase the contact angle of the LLDPE. We measured the contact angle of the water droplet on the porous LLDPE surface, and the average contact angle on the porous LLDPE surface is 153 ± 2°, indicating that a superhydrophobic LLDPE surface was obtained. From the water contact angle data on the smooth and porous LLDPE surfaces, the f2 calculated using equation (1) is about 0.862. This means that air occupies about 86.2% of the contact areas when the porous LLDPE surface forms contact with the water droplet, which is responsible for the superhydrophobic property. This kind of porous surface structure that can trap air is beneficial to a low sliding angle [47]. Results show that the sliding angle of the as-prepared superhydrophobic LLDPE surface is only 10°, indicating that water droplets can roll easily on the as-prepared superhydrophobic LLDPE surface. From the SEM images shown in figure 1 and other experimental observations, we can explain the possible formation of the porous superhydrophobic LLDPE surface as follows: in general, the polymer solution becomes thermodynamically unstable when drying the solution under certain conditions. As a result, phase separation occurs to form a polymer-rich phase and a polymer-poor phase. The concentrated phase solidifies after phase separation and forms a matrix, whereas the polymer poor-phase forms pores [48]. When the LLDPE solution was dried at 120 °C, the temperature was so high that the solvent evaporated quickly, preventing phase separation. Therefore, a smooth LLDPE film was formed (shown in figure 1(a)). When the LLDPE solution was dried at 5 °C, the solvent evaporation rate was low, phase separation occurred, and rough surfaces were formed (shown in figure 1(b)). Note that ethanol does not dissolve LLDPE. Thus, when ethanol was added to the LLDPE solution, ethanol acted as a precipitator, and some LLDPE aggregates appeared. The precipitated polymer (LLDPE) acted as a nucleus and the polymer-rich phase preferred to aggregate around this nucleus in order to decrease surface tension [8]. Thus, phase separation was promoted further, which led to the formation of a rough porous superhydrophobic LLDPE surface structure (shown in figure 1(c)).

Using a similar method, Lu et al [44] obtained a superhydrophobic LDPE composed of microflowers by adding cyclohexanone to a LLDPE solution. However, cyclohexanone has a very low evaporation velocity because of its high boiling point (155.7 °C), and the evaporation time of the mixed solvents used to obtain a superhydrophobic surface is very long. Here, we added some ethanol, which has a lower boiling point (~78 °C) to the LLDPE solution and obtained a porous superhydrophobic LLDPE surface. Compared with the study by Lu et al [44], our preparation time is much shorter, which is beneficial for manufacturing. In addition, previous reports on superhydrophobic LDPE focused only on the preparation process and paid little attention to the evaluation of the self-cleaning property, stability and suitability for other liquids such as corrosive liquids [16, 44]. Here, we studied the self-cleaning property and wettability of corrosive liquids and the stability of the as-prepared superhydrophobic LLDPE surface.

Natural superhydrophobic species have excellent self-cleaning property [3]. However, studies of the self-cleaning property of artificial superhydrophobic surfaces are few [49]. Here, we investigated the self-cleaning property of both the as-prepared superhydrophobic and smooth LLDPE surfaces by a method similar to Barthlott’s method [3]. We used ZnO (5–20 µm), CaCO3 (10–50 µm), and CO3O4 (5–30 µm) as contaminant particles. The samples were placed in a contamination chamber consisting of a frame measuring 30 × 30 × 80 cm covered with plastic foil. The chamber was divided by a removable horizontal wooden plate, placed 20 cm above the ground, covering the specimens. The contaminants were blown into the upper part of the contamination chamber by pressured air. After 10s, the wooden plate was removed. Subsequently, the particles evenly deposited on the specimens. After contamination, the specimens were tilted by about 10° and subjected to artificial rain produced by a sprinkler with an average pore diameter of 2 mm. After rinsing the samples for 3 min using the artificial rain, the samples were dried at 50 °C to remove residual water droplets. The number of particles on the specimens was determined by SEM. Figure 2 shows the residual contamination on both the as-prepared superhydrophobic and smooth LLDPE surfaces. Artificial rain removed 99% of the contaminant particles on the superhydrophobic LLDPE surface. However, 30% of the contaminant particles remained on the smooth LLDPE surface, indicating that the self-cleaning property of the as-prepared superhydrophobic LLDPE surface is better than that of the smooth LLDPE surface. We also immersed the superhydrophobic LLDPE surface for 15 days in dirt water containing natural soil, and no contamination was observed.
showing excellent self-cleaning property. We can explain the self-cleaning property of the porous superhydrophobic LLDPE surface as follows: The real contact areas of both water droplets and contaminant particles with the LLDPE solid were very small because trapped air occupied about 86.2% of the porous superhydrophobic LLDPE surface. Thus, the superhydrophobic LLDPE surface showed low adhesive force for both water droplets and contaminant particles. The very small contact areas and low adhesive force caused water droplets to roll easily and fast by gravity, and the kinetic energy was high. Therefore, the contaminant particles on the superhydrophobic LLDPE surface were captured, carried away, and removed from the superhydrophobic LLDPE surface when the contaminant particles met the water droplets with high kinetic energy, which overcame the adhesive force between the LLDPE solid and the contaminant particles. However, on the smooth LLDPE surface, the contact areas of both water and contaminant particles with the LLDPE solid were much larger, and accordingly the adhesive force of the smooth LLDPE surface for both the water droplets and the contaminant particles were also higher. The higher adhesive force and larger contact areas caused the water droplets on the smooth LLDPE surface to slide slowly, and the kinetic energy was low, which made it difficult to overcome the adhesion between the contaminant particles and the LLDPE surface. In this case, only the contaminant particles with adhesive force between the water droplets and the particles stronger than the adhesive force between the LLDPE and the particles were removed by the water droplets; the other contaminant particles remained on the smooth LLDPE surface [3]. Note that more contaminant particles on the smooth LLDPE surface could be removed if the surface is subjected to heavy rain having larger droplet size and kinetic energy.

In most previous studies, the wettability of superhydrophobic surfaces was evaluated using pure water only; only a few studies have examined the wettability of other liquids such as corrosive liquids on superhydrophobic surfaces. Here, we studied the wettability of different liquids with pH ranging from 1 to 14. Figure 3 shows the relationship between pH and water contact angle on the as-prepared superhydrophobic LLDPE surface. Interestingly, the as-prepared superhydrophobic LLDPE surface shows superhydrophobicity in the pH range 2–13. That is, the water contact angles are larger than 150° for not only pure water but also corrosive liquids such as acidic and basic aqueous solutions. There is no evident fluctuation in water contact angle on the superhydrophobic LLDPE surface within experimental error when pH is changed from 2 to 13. However, when the pH is lower than 2 or larger than 13, the contact angles are lower than 150°; for example, it is 146° for pH = 1. These results are important for applications of superhydrophobic LLDPE in corrosive liquids.

In addition, we also studied the durability of the superhydrophobic LLDPE surface by several methods. The samples were stored in ambient for one month, and water contact angle was measured at different intervals. Interestingly, their water contact angle and sliding angle remained constant, indicating the long-term stability of the LLDPE superhydrophobicity. To assess thermal stability, superhydrophobic LLDPE was placed in an oven for a 30 min treatment at different temperatures ranging from 10 to 90 °C. The water contact angles of the superhydrophobic LLDPE surface remained constant for these annealing temperatures.

4. Conclusions

In summary, we prepared a porous, stable superhydrophobic LLDPE surface by a simple method, which can also be applied to produce other superhydrophobic surfaces. The superhydrophobic LLDPE surface exhibits excellent self-cleaning property compared with the smooth LLDPE surface. The superhydrophobic LLDPE surface shows high stability in the pH range from 2 to 13. When the LLDPE samples were stored in ambient environment for one month, their water contact angle and sliding angle remained constant. The superhydrophobic property was also unchanged by annealing in the temperature range 10–90 °C. Those properties might result in numerous industrial and agricultural applications of superhydrophobic LLDPE.
Acknowledgments

The authors acknowledge the support of the Natural Science Foundation of China (no. 60571001); and the Natural Science Foundation of Hunan province (no. 04jj40023).

References

[1] Ma M and Hill R M 2006 Corr. Opin. Colloid Interface Sci. 11 193
[2] Onda T, Shibuchi S, Satoh N and Tsujii K 1996 Langmuir 12 2125
[3] Barthlott W and Neinhuis C 1997 Planta 202 1
[4] Yuan Z, Chen H, Tang J, Gong H, Liu Y, Wang Z, Shi P, Zhang J and Chen X 2007 J. Phys. D: Appl. Phys. 40 3485
[5] Gao X and Jiang L 2004 Nature 432 36
[6] Li X, Reinhoudt D and Crego-Calama M 2007 Chem. Soc. Rev. 36 1350
[7] Nakajima A, Fujishima A, Hashimoto K and Watanabe T 1999 Adv. Mater. 11 1365
[8] Erbli H Y, Demirel A L, Avci Y and Mert O 2003 Science 299 1377
[9] Shirtcliffe N J, McHale G, Newton M I, Perry C C and Roach P 2007 Mater. Chem. Phys. 103 112
[10] Hegde N D, Hirashima H and Rao A V 2007 J. Porous Mater. 14 165
[11] Rao A V, Kulkarni M M and Bhagat S D 2005 J. Colloid Interface Sci. 285 413
[12] Hikita M, Tanaka K, Nakamura T, Kajiyama T and Takahara A 2005 Langmuir 21 7299
[13] Teshima K, Sugimura H, Inoue Y, Takai O and Takano A 2004 Chem. Vapor. Depos. 10 295
[14] Zhang Y, Kang E T, Neoh K G, Huang W, Huan A C H, Zhang H and Lamb R N 2002 Polymer 43 7279
[15] Tserepi A D, Vlachopoulos M E and Gogolides E 2006 Nanotechnology 17 3977
[16] Fresnais J, Chapell J P and Poncin-Epaillard F 2006 Surf. Coat. Technol. 200 5296
[17] Vourdas N, Tserepi A and Gogolides E 2007 Nanotechnology 18 125304
[18] Jiang L, Zhao Y and Zhai J 2004 Angew. Chem. Int. Ed. Engl. 43 3338
[19] Zheng J, He A, Li J, Xu J and Han C C 2006 Polymer 47 7095
[20] Acatay K, Simsek E, Ow-Yang C and Menceloglu Y Z 2004 Angew. Chem. Int. Ed. Engl. 43 5210
[21] Ma M, Hill R M, Lowery J L, Fridrikh S V and Rutledge G C 2005 Langmuir 21 5549
[22] Lim J, Yi G, Moon J H, Heo C and Yang S 2007 Langmuir 23 7981
[23] Zhu Y, Feng L, Xia F, Zhai J, Wan M and Jiang L 2007 Macromol. Rapid Commun. 28 1135
[24] Zhu Y, Zhang J, Cheng Y, Huang Z, Feng L and Jiang L 2006 Adv. Funct. Mater. 16 568
[25] Zhu M, Zuo W, Yu H, Yang W and Chen Y 2006 J. Mater. Sci. 41 3793
[26] Jin M, Feng X, Feng L, Sun T, Zhai J, Li T and Jiang L 2005 Adv. Mater. 17 1977
[27] Puukilainen E, Rasilainen T, Suvanto M and Pakkanen T A 2007 Langmuir 23 7263
[28] Zhang L, Zhou Z, Cheng B, DeSimone J M and Samulski E T 2006 Langmuir 22 8576
[29] Shang H M, Wang Y, Takahashi K, Cao G Z, Li D and Xia Y N 2005 J. Mater. Sci. 40 1358
[30] Jisr R M, Rmaile H H and Schlenoff J B 2005 Angew. Chem. Int. Ed. Engl. 44 782
[31] Zhai L, Cebeci F C, Cohen R E and Rubner M F 2004 Nano Lett. 4 1349
[32] Zhang X, Shi F, Yu X, Liu H, Fu Y, Wang Z, Jiang L and Li X 2004 J. Am. Chem. Soc. 126 3064
[33] Shi F, Wang Z and Zhang X 2005 Adv. Mater. 17 1005
[34] Zhao N, Shi F, Wang Z and Zhang X 2005 Langmuir 21 4713
[35] Khorasani M T, Mirzadeh H and Kermani Z 2005 Appl. Surf. Sci. 242 339
[36] Pozzato A, Dal Zilio S, Fois G, Vendramin D, Mistura G, Belotti M, Chen Y and Natali M 2006 Microelectron. Eng. 83 884
[37] Lee E J, Lee H M, Li Y, Hong L Y, Kim D P and Cho S O 2007 Macromol. Rapid Commun. 28 246
[38] Favia P, Cicala G, Milella A, Palumbo F, Rossini P and d’Agostino R 2003 Surf. Coat. Technol. 169–170 609
[39] Zhang H, Lamb R and Lewis J 2005 Sci. Technol. Adv. Mater. 6 236
[40] Yuan Z, Chen H, Tang J, Chen X, Zhao D and Wang Z 2007 Surf. Coat. Technol. 201 7138
[41] Xue C H, Jia S T, Chen H Z and Wang M 2008 Sci. Technol. Adv. Mater. 9 035001
[42] Xue C H, Jia S T, Zhang J, Tian L Q, Chen H Z and Wang M 2008 Sci. Technol. Adv. Mater. 9 035008
[43] Li G, Wang B, Liu Y, Tan T, Song X, Li E and Yan H 2008 Sci. Technol. Adv. Mater. 9 025006
[44] Lu X, Zhang C and Han Y 2004 Macromol. Rapid Commun. 25 1606
[45] Wenzel R N 1936 Ind. Eng. Chem. 28 988
[46] Cassie A B D and Baxter S 1944 Trans. Faraday Soc. 40 546
[47] Miwa M, Nakajima A, Fujishima A, Hashimoto K and Watanabe T 2000 Langmuir 16 5754
[48] Zhao N, Xu J, Xie Q, Weng L, Guo X, Zhang X and Shi L 2005 Macromol. Rapid Commun. 26 1075
[49] Fürstner R, Barthlott W, Neinhuis C and Walzel P 2005 Langmuir 21 956