Huanhuan Feng, Tingting Zheng, Huiliang Wang*

Biomimetic Superhydrophobic Polyolefin Surfaces Fabricated with a Facile Scraping, Bonding and Peeling Method

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Abstract: Inspired by the superhydrophobicity of juicy peach surface, on which microscale hairs are standing vertically to the surface plane, an extremely simple, inexpensive physical method is developed for fabrication of superhydrophobic polyolefin surfaces over large areas. This method includes three steps: abrasive paper scraping, adhesive tape bonding and 90° peeling. Scraping increases the roughness and enhances water contact angles (CAs) on polyolefin surfaces. It increases more when the scraped surface are bonded with adhesive types and then then 90° peeled. The CA variation depends on the types of polyolefin and abrasive paper. Superhydrophobic low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) surfaces (CA>150°) are obtained and they all exhibit very low adhesive force and high resistance to strong acids and bases.

Keywords: superhydrophobic, contact angle, water repellent

Introduction

Superhydrophobicity is a fairly common phenomenon in nature[1-5]. Otten and Herminghaus have revealed that there are at least two distinctly different types of water-repellent plant leaves [6]. The first type is macroscopically smooth leaves such as lotus, and their superhydrophobicity is attributed to the micro- and nanometer-scale hierarchical structures together with hydrophobic epicuticular wax crystalloids [7]. Up to now, most of the work on artificial superhydrophobic surfaces focuses on mimicking the micro- and nanometer-scale hierarchical structures of lotus leaves, and many chemical and/or physical methods have been developed [8-19]. The second type is hair covered leaves such as the Lady’s Mantle and their superhydrophobic properties that rely on the long and flexible microscale hairs [6]. Besides plant leaves, some fruit surfaces are also covered with hairs. In this work, we will present that hairs covered juicy peach surfaces also demonstrate superhydrophobicity. Nevertheless, much less attention has been paid to the theoretical and experimental studies on superhydrophobic surfaces with microscale hairs [20-24].

Polyolefins, such as polyethylene (PE) and polypropylene (PP), are the most widely used plastics. They are generally very resistant to many chemicals, e.g. salts, acids, bases, alcohols, and even petrol. Superhydrophobic polyolefins have many practical applications. There are several methods to obtain superhydrophobic polyolefin surfaces, such as crystallization control [25], molding, [26-28], plasma treatment [29-32], solution coating [33], pulsed laser deposition [34] and so forth. We have also fabricated superhydrophobic high-density polyethylene (HDPE) surface through the photografting method [35]. Most of the superhydrophobic polyolefin surfaces have micro- and nano-sized hierarchical structures. These methods are usually multistep, difficult to control, and expensive and therefore, developing simple and low-cost methods to fabricate superhydrophobic surfaces are of important practical significance.

In recent years, increasingly efforts have been devoted to fabricate superhydrophobic polymeric surfaces with microscale hairy structures. The microscale hairy structures are generally fabricated by template assisted processes [22, 23, 36, 37]. For example, Hsu et al. [23] reported hydrophobic interface mimicking hairs of arthropods made via a membrane casting technique on polypropylene substrates. Lee et al. [36] fabricated
a hard-polymer-based adhesive formed with high-aspect-ratio microfibers from HDPE by thermal molding using a Polycarbonate (PC) template with holes. Ye et al. [38] fabricated highly reflective superhydrophobic white coating inspired by poplar leaf hairs using coaxial electro-spinning technology. Zhao et al. [24] developed a facile process for fabricating various hairy carbonaceous fiber structures with a low-temperature chemical vapor deposition (CVD) process. And very recently, Zhang et al. [39] reported the fabrication of superhydrophobic polyolefin surface by unzipping a polymer film, which is prepared by the thermal lamination of a HDPE film and a PP/HDPE blend film. The unzipped surface of the PP/HDPE blend shows a rough morphology consisting of nano- or submicron sized fibrous textures (hairs).

One of the most convenient and effective methods for fabricating superhydrophobic polyolefin surfaces was reported by Gao et al., who used abrasive paper to scrape the polymer surfaces [40]. Scraping increases the surface roughness of polymeric materials and thereafter alters the water contact angles (CAs). According to Gao et al., the polymers with CAs ranging from 65° to 90° on their smooth surfaces exhibited enhanced hydrophobicity after scraping, and superhydrophobic surfaces could be obtained with poly(dimethylsiloxane) and poly(tetrafluoroethylene), but not with PE and PP [40].

The theoretical study by Blow and Yeomans [20] show that the incline of an array of hairs strongly affect their effectiveness in supporting a liquid away from the base substrate. Actually, the natural and artificial hairy superhydrophobic surfaces usually have vertically aligned micro- or nanopillar arrays. The scraping method produces microscale hairs or thin slices on the polymeric surfaces, but they are mostly inclined or flattened due to the shear force and pressure during scraping [40]. Therefore, if the microscale hairs or thin slices can be vertically aligned, the CAs on the polymer surfaces can be further enhanced and very possibly superhydrophobicity can be obtained for more polymers.

We found that when the scraped surfaces were bonded with adhesive tapes and then 90° peeled off, the CAs on polyolefin surfaces increased significantly. Superhydrophobic HDPE, low-density polyethylene (LDPE) and polypropylene (PP) surfaces were obtained with this extremely simple scraping, bonding and peeling method.

### Experimental

#### Materials

High-density polyethylene (HDPE, Type 4000s), low-density polyethylene (LDPE, Type 100AC) and polypropylene (PP, Type 2401) were supplied by Yanshan Petrochemical Co., Ltd., Beijing, China. The polyolefin grains or powders were hot-pressed into thin sheets (ca. 400-500 µm in thickness). The abrasive papers (Panda brand) were made by Beijing Dongxin Abrasion Tools Co., Ltd., Beijing, China, and follow the European FEPA (Federation of European Producers of Abrasives) standard. Six types of abrasive papers made with Al₂O₃ were used. Their grit designations and average particle diameters (in µm) are P80 (201), P280 (52.2), P360 (40.5), P1000 (18.3), P1500 (12.6) and P2000 (10.3), respectively. Commercial adhesive tapes and juicy peaches were purchased from market.

#### Fabrication method

The surface of polyolefin sheet was manually scraped with an abrasive paper circularly for about 20 times. After scraping, the scraped surfaces were bonded with commercial adhesive tapes tightly and then the adhesive tapes were 90° peeled off.

#### Contact angle measurement

Contact angle measurement were determined using a DataPhysics OCA20 contact-angle system (Germany) at ambient humidity and temperature. Droplets of deionized water were placed at different locations on the samples using a micro-syringe. The droplet volume was 3 µL. A minimum eight readings was taken for each sample in order to determine average values.

#### SEM characterization

The SEM micrographs of the PE and PP surfaces were obtained with Hitachi S-4800 cold field emission scanning electron microscope (Tokyo, Japan) with an accelerating voltage of 10 kV. The samples were sputter coated with gold.
Results and discussion

Superhydrophobic juicy peach surface

Fig. 1 shows the SEM micrograms of the surface of a juicy peach and the hairs showing superhydrophobicity. There are many hairs with diameters in the range of 10-20 µm and lengths varying from several tens micrometers to about 1 mm. Most of the short hairs are standing vertically to the surface plane, while the long ones are flattened. The water CAs on juicy peach surfaces are generally more than 150° and the one shown in the inset of Fig. 1 was 153°, confirming the juicy peach surface is superhydrophobic. We have measured the water CAs with several types of hairs covered juicy peaches and found that their surfaces were superhydrophobic. It has to be mentioned that some types of peaches do not have hairy surfaces and therefore they do not show superhydrophobicity.

Despite peaches are very common fruits, we have not found any reports on the superhydrophobicity of juicy peach surfaces. Clearly, the superhydrophobicity of juicy peach surface belongs to the second type revealed by Otten and Herminghaus and the superhydrophobic property relies on the microscale hairs [6]. When the hairs on a juicy peach were flattened with external forces, the peach surface lost its superhydrophobicity. This fact indicates that the orientation of the microscale hairs is a very important factor for the wetting properties of juicy peach surface.

Fabrication process

Inspired by the superhydrophobicity of juicy peach surface, we believe that if we can mimic the hairy microstructure from the juicy peach surface, then maybe we can obtain superhydrophobic surfaces. We selected LDPE, HDPE and PP as the polymer substrates. As mentioned in the introduction, scraping can increase the roughness on polyolefin surface; however, it is not enough to achieve superhydrophobicity on polyolefin surfaces. Therefore, further treatments on scraped surfaces are necessary.

The fabrication process is shown in Fig. 2. The surface of polyolefin sheet was scraped with an abrasive paper first. We used abrasive papers with different grit sizes to scrape the sheets with hand. With the increase of scraping times, the roughness of the surface increased and the semi-transparent polyolefin sheet became opaque. It was found that scraping the surfaces circularly for about 20 times was enough to reach the maximum CAs, further scraping would not increase the CAs. After scraping, the surfaces were tightly bonded with commercial adhesive tape and then the adhesive tape was 90° peeled off.

Superhydrophobicity of the treated polyolefin surfaces

The original water CAs on the surfaces of pristine HDPE, LDPE and PP sheets were 92.5±3.0°, 94.6±2.5° and 85.2±5.8°, respectively. The CAs on the surfaces after each treatment are shown in Fig. 3. The CAs on the scraped polyolefin sheets increased with the grit designation of abrasive paper, and then decreased. For HDPE samples, the maximum CAs reached about 143° when using the abrasive papers P280 and P360; for LDPE samples, the maximum CA reached 138° when using the abrasive paper P280; and for PP samples, the maximum CAs was approximately 150° when using the abrasive paper P360. These results are similar to those obtained by Gao et al. [40].

After being bonded and peeled, the CAs on all the samples increased, and the CAs on the bonded and peeled surfaces also increased with the grit designation of abrasive paper, and then decreased. For HDPE samples, the CAs were more than 150° when using the abrasive papers P80, P280, P360 and P1000; for LDPE samples, the maximum CA was 156.8±3.5° when using the abrasive
paper P360; and for PP samples, the CAs were more than 150° when using the abrasive paper P80, P280 and P360.

The maximum CA shift for the samples after being bonded and peeled depends on the nature of the polyolefin and the abrasive paper used. For HDPE and LDPE samples, there were about 50° or more CA increase when using the abrasive paper P1000; but for PP samples, the maximum CA shift was only about 16° when using the abrasive paper P280.

Fig. 4 shows the digital photos of water droplets on HDPE surface after being treated with scraping, bonding and peeling. In all cases when measuring the CAs, the suspending droplets were very difficult to pull down to the surface. Water droplets could slide easily on the surfaces when there was a very small angle (normally less than 5°), indicating the superhydrophobic surfaces had a very low tilting angle. These results indicate that superhydrophobic HDPE, LDPE and PP surfaces can be obtained by a simple scraping, bonding and peeling method.

A superhydrophobic surface usually associates with a low adhesive force. Fig. 5 shows the photos taken to measure the CA of a treated LDPE surface. The PE substrate was lifted to obtain contact with the water droplet suspended on a microsyringe. When the PE substrate was dropped the water droplet could not to be pulled down to the superhydrophobic surface, instead it departed from the lowering surface easily without any of the droplet remaining (Fig. 8d), suggesting that the adhesive force between the surface and water is much lower than that between the microsyringe and the water droplet. Similar phenomena were observed for the superhydrophobic HDPE and PP surfaces. This experiment shows that the superhydrophobic polyolefin surfaces obtained by a scraping, bonding and peeling method also exhibit very low adhesive force.

Due to the intrinsic inert nature of polyolefins, they are generally very resistant to many chemicals. The CAs of water droplets were measured with different pH values on the obtained superhydrophobic surfaces. Fig. 6 shows the CAs of the PP surface craped with P360 abrasive paper and then bonded and peeled in a wide pH range. Not surprisingly, the CAs are generally more than 150° when the pH value ranges from 1 to 14, suggesting that the superhydrophobic surface is highly resistant to strong acids and bases.
Surface morphologies

Fig. 7 shows the top-view and cross-section SEM micrograms of HDPE surfaces after being scraped with the abrasive paper P360, and then being bonded and peeled. The scraped HDPE surface (Fig. 7a) was rough in comparison to the pristine smooth HDPE surface, and some chippings and hairs appeared. After being bonded and peeled, the chippings disappeared (Fig. 7c) and most of the hairs were erected (Fig. 7d). For the HDPE, LDPE and PP samples that were scraped with different types of abrasive paper, a similar erection of the hairs after bonding and peeling was observed. Fig. 8 shows the SEM micrograms of the scraped, bonded and peeled HDPE, LDPE and PP samples scraped with the abrasive paper P1000.
Discussion

As a simple physical process, the scraping, bonding and peeling method does not alter the surface energy but surface roughness of polyolefin. It is well known that, on the basis of Wenzel [41] and Cassie’s work [42], surface roughness has a profound influence on the wetting properties of a material. The CAs shift on polyolefin surfaces can be explained with Wenzel (1) and Cassie–Baxter (2) modes:

\[
\cos \theta_C = r \cos \theta \tag{1}
\]

\[
\cos \theta_C = f_s (1 + \cos \theta) - 1 \tag{2}
\]

where \( \theta_C \) and \( \theta \) are the water CAs on rough and smooth polyolefin surfaces, respectively; \( r \) is the roughness ratio which is defined as the ratio of true area of the solid surface to the apparent area; and \( f_s \) is the fraction of solid/liquid interface below the drop.

The scraping, bonding and peeling process increase the roughness of the surface and hence alter the \( r \) and/or \( f_s \), which strongly affect the exact values of CAs. Although, for these surfaces, it is difficult to know these parameters precisely, the SEM investigations (Figs. 7 and 8) could provide some qualitative structural information of the hairs formed on these surfaces.

After scraping, the hairs formed were usually flattened or slanting on the surface, the water droplet could wet most of the surface below it, and in this case Wenzel mode can be applied. Scraping induced the increase in roughness and thus the \( r \) of polyolefin surface, therefore increasing in CA. The shapes, numbers and lengths of the hairs formed on the scraped surfaces vary with the polyolefin and abrasive paper types, leading to differences in CAs. (i) The particle size of abrasive paper decreases with its grit designation; therefore, with the increase of grit designation, the diameter \( R \) and the length \( L \) of the hairs and the distance \( D \) between the hairs decreases. The simultaneous decrease in \( R, L \) and \( D \) with grit designation leads to a maximum \( r \). This is the reason for the CA first increases and then decreases with grit designation (Fig. 3 a-c). It has to be mentioned, for some scraped surfaces especially those scraped with lower grit designation abrasive papers (e.g., P280, P360), their CAs can reach 140° or more. If the CA increase is entirely attributed to the increase in roughness, then the \( r \) in Wenzel equation should be about 10-20, but it is difficult to conclude from the SEM micrograms (Fig. 7) that the \( r \) could be so high. The hairs in these cases are not horizontally flattened but slanting on the surfaces (Fig. 7b), therefore, very possibly, water can only wet a part of the solid surface below it and an intermediate state between the Wenzel and the Cassie modes might be applied for them. (ii) The chemical structures of LDPE, HDPE and PP are similar; all are composed of C-C and C-H bonds. Their mechanical and physical properties largely depend on their microstructures, such as chain length, branching, tacticity and crystallinity, etc. HDPE and LDPE differ in their chain length, branching and hence crystallinity. HDPE is composed of very long unbranched hydrocarbon chains which pack together easily in crystalline domains, and hence is relatively strong and stiff yet still retains a degree of flexibility. On the other hand, LDPE is composed of shorter and more highly branched chains, which do not easily adopt crystalline structures. It is therefore softer, weaker, less dense and more easily deformed than HDPE. Most commercial PP is isotactic and has an intermediate degree of crystallinity between that of LDPE and HDPE. Polypropylene is normally tough and flexible. The elastic modulus and hardness of the polyolefins used are in the order of LDPE<HDPE<PP. LDPE is the most flexible material used and its surface is the most difficult one to be scraped, hence there are always the fewest hairs formed on the surface and the hairs are usually horizontally flattened (Fig. 8c). HDPE and especially PP surfaces are easier to be roughened, and the hairs formed are usually slanting rather than horizontally flattened (Fig. 8e). These facts can explain why the CAs on the scraped polyolefin surfaces are generally in the order of PP>HDPE>LDPE when using the same abrasive paper.

When the scraped surface is bonded and peeled, the chippings are removed and the hairs are erected (Fig. 7c, d and Fig. 8b, d, f). The removal of chippings decreases the roughness, leading to the decrease in CA if Wenzel mode works. By contrast, the CA increase is observed for all samples (Fig. 3). This implies that Cassie mode or an intermediate state between the Wenzel and the Cassie modes applies in this case. The erection of the hairs increases their apparent heights, and then the water drop can only wet the very small top area rather than the much bigger side area of the hairs (Cassie mode) or only a part of the solid surface below it (intermediate state). Both cases lead to CA increase. After being bonded and peeled, there is 50° or more CA increase for HDPE and LDPE surfaces scraped with the abrasive paper P1000, but no so significant CA increase has been observed for PP sample (Fig. 3). The explanations are: (i) the hairs formed on HDPE and LDPE are horizontally flattened (Fig. 8), and the bonding and peeling process could significantly increase their apparent heights, inducing the change from Wenzel mode to Cassie mode; (ii) due to the high modulus of PP,
the smaller and shorter hairs are usually slanting and are easy to be damaged by further scraping, as evidenced by the fact that there are less hairs on PP than on HDPE surface (Fig. 8), this leads to the increase in contact area for water and the decrease in CA.

From the results and discussion above, we can conclude that the erection of the microscale hairs is essential for the superhydrophobicity of the scraped polyolefin surfaces, the same for the juicy peach surface and other superhydrophobic surfaces that belong to the second type of water repellent surfaces.

This scraping, bonding and peeling method is a further development of the scraping method reported by Jiang et al. [40]. The bonding and peeling processes could erect the hairs and hence increase the water CAs on the scraped surfaces.

It has to be pointed out that we scraped the polyolefin sheets by hand, and therefore the pressures on the polymer substrates during scraping were not quantitatively recorded. However, we have tried to scrape the polyolefin sheets by several people with different forces, and very similar results were obtained. It has been mentioned in the Fabrication process section of this paper that the samples used for CA measurements were scraped “circularly” for about 20 times. The only purpose is to emphasize that we prepared the samples in the same way for avoiding random errors arising from different scraping directions. Results indicate, the scraping can be done in any direction.

We have also tried to bond the scraped surfaces with different commercial adhesive tapes and found that all of them worked comparably. The speed of 90° peeling of the bonded adhesive tape would not affect the final wetting property of the polyolefin surface either. The main function of bonding and peeling processes is to erect the flattened or slanting hairs. As the polyolefins used are flexible polymers, the hairs on their scraped surfaces are easily erected by 90° peeling if they are bonded with the adhesive tape even when the adhesion is not strong.

Transparent adhesive tape has a transparent film backing and an acrylic or synthetic rubber based adhesive. The polyolefin surfaces might be contaminated by the adhesive layer from adhesive tape during the bonding and peeling processes. However, from the SEM observations (Figs. 7 and 8), no agglomeration of peeled adhesive can be found on the treated surfaces. As PE and PP consist of just C and H they can only interact with adhesive by Van der Waals bonds, there is no possibility of forming strong adhesion between polyolefins and adhesive. Therefore, no adhesive is peeled off from the adhesive tape and left on the polyolefin surfaces.

The superhydrophobic polyolefin surfaces treated with the scraping, bonding and peeling method had some distinct features. (i) Due to the inert chemical structures of the polyolefins, the as-prepared surfaces show superhydrophobicity even for corrosive aqueous solutions. Unfortunately, due to the hydrophobic nature of polyolefins, the as-prepared surfaces do not show superhydrophobicity to organic solvents such as alcohols and petroleum. (ii) Their superhydrophobicity can be easily recovered by repeating the bonding and peeling process once the hairs on them are flattened by external forces and the polyolefin sheets can be used for many times by simply repeating the fabrication process.

Conclusions

In conclusion, we have fabricated superhydrophobic polyolefin surfaces through a physical method-scraping, bonding and peeling. It is extremely simple and does not require any expensive chemicals and equipment. The fabrication of superhydrophobic polyolefin surfaces over large areas can be easily achieved with conventional abrasion machines. This method can be applied to other hydrophobic polymeric materials to achieve superhydrophobicity. We believe, due to its easiness and low cost, this fabrication method may find some practical applications.

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