A Self-Assembly and High-Robustness Super-Hydrophobic Coating Based on Waste Marble Powder

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Uncontrolled waste marble powder contributes negatively to the environment. This paper reports a cheap and facile method to prepare a super-hydrophobic self-cleaning coating with high-robustness by using waste marble powder as the basic components. The PFOTES (1H,1H,2H,2H-Perfluoroctyltrihexosilane) was selected as the modification agents which is self-assembled on the marble powder surface. A very low mass concentration of PFOTES (0.1208% wt.) increases the water contact angle of a coated sample from 11.5° to 138°. With the gradual increase of PFOTES, the water contact angle increases from 138° to 153°. The sliding angle value, however, varies from over 180° (the water droplet will not fall even it is turned upside down) to 6.8°, which represented the wetting model changing from Wenzel model to the Cassie-Baxter model. Thus, the super-hydrophobic self-cleaning coating is obtained. Besides, the coating showed an excellent robustness, no obvious contact angle and sliding angle differences were detected after 10 times’ robustness test (the contact angle and sliding angle ranged from 147° to 155° and 6.8° to 8.5° respectively). [doi:10.2320/matertrans.M2016255]

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1. Introduction

Marble is a quite widely used construction material all around the world. However, during the polishing and sawing process of marble slab in factories, tremendous waste marble powder is produced. The waste marble powder has been treated as one of the series pollutants because its basic elements are composed of micron/submicron CaCO$_3$ and CaSiO$_3$, which is easy to be inhaled by the human body and causes serious lung diseases. Besides, the marble powder can also pollute ground water and soil if stone factories directly discharge the slurry containing marble powder into the environment. Consequently, the awareness of such problems has recently stimulated by the local environmental department and more and more investigations regarding the reuse of the waste marble powder have been conducted.

At present, the main application of waste marble powder is to enhance the mechanical properties of cement and concrete by adding waste marble powders. For example, Aliabdo et al. measured the properties of cement modified with waste marble powder and they found that if the marble powder content was 10.0%, the compressive strength was increased by 9%. Moreover, if the marble powder replaced 10% of the sand in the concrete, the splitting tensile strength increased by about 16%. Corinaldesi also reported that concrete achieved at maximum compressive strength when 10% of sand was substituted by marble powder. Furthermore, N.Bilgin et al. reported the use of waste marble in the brick industry and they reported that the hardness of the brick increased in parallel with marble powder content.

However, only a few attentions are focused on the application of such waste materials to produce environmental friendly paint. Hence, different from the previous research, this paper reported a brand new strategy for waste marble powder application: a novel super-hydrophobic coating based on waste marble powder through a cheap and facile self-assembly method. Among most of the hydrophobic agent such as steric acid, PDMS, TEOS etc. PFOTES is selected as the super-hydrophobic agent because of its excellent super-hydrophobicity deriving from the massive of C-F groups. The schematic reaction diagram is illustrated in Fig. 1. First, the -Si-O-CH$_2$CH$_3$ groups in PFOTES are hydrolyzed into -Si-OH and then dehydrated with the -OH groups on the marble powder surface, which is a self-assembled process. Second, the surface modified marble powder is bonded on the substrate surface by 3M double-sided adhesive tape. Through the spray procedure, a super-hydrophobic self-cleaning coating is made as lotus surface. It also displayed an excellent robustness property after the related tests. Such coating can be considered to be used in many diverse fields, including self-cleaning coatings for external walls and microfluidics and it was also an effect way to reuse the waste marble powder.

2. Experimental Procedure

The waste marble powder was obtained from Nanan Building Materials Import and Export Company in Fujian Province, China. The powder was used without pretreatments. PFOTES and absolute ethyl alcohol were bought from Sigma-Aldrich. They were both of analytical grade and do not need further purification.

In this paper, a series of mixtures with different ratios between the contents of the PFOTES in the coating solution and the waste marble powder were made. To simplify the experi-
ments, the mass of marble powder was kept constant at 12 g, while the volume of PFOTES ranged from 0 μL to 100 μL. The density of PFOTES is measured by 1.4496 g/ml. The scope of the samples is given in Table 1. After the waste marble powder is settled in a beaker with 50 ml absolute ethyl alcohol, the PFOTES is added. It is then stirred at 400 r/min for 2 h. The modified waste marble powder is obtained after drying.

3. Characterizations

The FT-IR spectrums were got by the NicoletTM iSTM 50 FT-IR Spectrometer from Thermo Scientific. The water contact angle and sliding angle values were obtained by the Contact Angle Goniometer Sindatek Model 100SB from SINDATEK.

4. Results and Discussions

4.1 The FT-IR characterization of modified waste marble powder

Generally speaking, the self-assembling process of PFOTES occurs only on particle’s surface and thus the amount of PFOTES is extremely low. The FT-IR signal of the characteristic peaks, therefore, is so weak that they cannot be detected in relation to the strong peaks of CaCO3, especially given its huge concentration. In order to make the FT-IR signal as strong as possible, the original waste marble powder is set as the background in the FT-IR test. Further, the mass of the detected original waste marble powder was weighed precisely during the background test. The ”to-be-detected” modified waste marble powder should have that exact same mass. In this manner, the background noise can be eliminated to the maximum. The FT-IR spectrum for sample 11 is shown in Fig. 2.

![Fig. 1](image_url)

Fig. 1 The schematic diagram of the surface modification of waste marble powder.

![Table 1](table_image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOTES/μL</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Waste marble powder/g</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The mass ratio of PFOTES/%</td>
<td>0</td>
<td>0.1208</td>
<td>0.2416</td>
<td>0.3624</td>
<td>0.4832</td>
<td>0.604</td>
<td>0.7248</td>
<td>0.8456</td>
<td>0.9664</td>
<td>1.0872</td>
<td>1.208</td>
</tr>
</tbody>
</table>

The FT-IR spectrum for sample 11, which possesses the highest PFOTES concentration among all the samples, the figure demonstrates that such kind of modification does occur. The differences of PFOTES’s concentration in other samples are only quantitative variations. The water contact angle tests, described below, also show the hydrophobicity effects after the modification obviously, although its signal is very weak in FT-IR spectrum.

4.2 Water contact angle characterizations

After the FT-IR tests, the water contact angles of the samples were measured. Since the super-hydrophobicity is related to the surface roughness, the SEM image of modified waste marble powder is shown in Fig. 3. As shown in this figure, the waste marble powder has a small size, which ranges from 1–10 μm. Therefore, the roughness is at a relatively high level.

For the contact angle test, the super-hydrophobicity is so obvious that it can be observed by naked eyes. Figure 4 is a chart describing the influence of PFOTES’s concentration on the contact angle value. From Fig. 4 above, it can be seen clearly that firstly, a very small amount of PFOTES (0.1208% wt.) causes a big hydrophobic change: from 11.3° to 138°. Because the material on marble powder surface is modified, only a small amount of PFOTES is required. For the sample with a 0% PFOTES, the representation of CaCO3 because the balance cannot be so precise that the CaCO3 signal is eliminated completely. The double-peaks at 2360 cm⁻¹ are the characteristic peaks of CO2. This could be caused by human exhalation during the settling of the samples. The peaks at 2986 cm⁻¹ and 2879 cm⁻¹ are the stretching vibration band of C-H, which was probably caused by the impurities of PFOTES. The peaks at 1240 cm⁻¹ and 1143 cm⁻¹ represent the C-F groups. Thus, it is reasonable to believe that the PFOTES is grafted onto the marble’s surface.

Even though Fig. 2 is the FT-IR spectrum for the sample 11 only, which possesses the highest PFOTES concentration among all the samples, the figure demonstrates that such kind of modification does occur. The differences of PFOTES’s concentration in other samples are only quantitative variations. The water contact angle tests, described below, also show the hydrophobicity effects after the modification obviously, although its signal is very weak in FT-IR spectrum.
contact angle is 11.3°. This is because the marble powder is hydrophilic, and additionally, the marble powder coating on the glass substrate forms a loose surface structure with multiple gaps contributing greatly to the water absorption. Secondly, with the gradual increase of the PFOTES the water contact angle gains slowly from 138° to 153°. However, the differences between the contact angle pictures are not obvious, thus only three of them (Sample 2, Sample 6 and Sample 11) are displayed. It seems that when the ratio of PFOTES reaches a certain level (0.1208% wt.), its contribution to an increase in water contact angle becomes not so obvious. This phenomenon is explained later. Besides that, although the differences in water contact angles are small, there are some other obvious differences in sliding angle values, which is demonstrated below.

### 4.3 Water sliding angle characterizations

Even though there is only a slight water contact angle change with the increase of PFOTES, the sliding angle values change greatly as shown in Fig. 5.

It is obvious from Fig. 5 that with an increase of PFOTES content, the water sliding angle decreases gradually. When the ratio of the PFOTES is 0.1208% wt., the sliding angle is so big that water droplets do not move even when the glass...
sheet is turned upside down. This phenomenon (a surface with relatively high water contact angle but extremely big sliding angle) is called the "petal effect". There is another phenomenon called the "lotus effect", which is the case of huge contact angle along with a small sliding angle. Those two kinds of effects are represented by two models: Wenzel model and Cassie-Baxter model. They are shown in Fig. 6.

The formula describing the relation of contact angle and roughness is as follows:

\[ \cos \theta' = f \cos \theta + (1 - f) \cos \pi = f \cos \theta - (1 - f) (1) \]

where \( f \) is an area fraction of the solid-liquid interface and \((1 - f)\) is that of the solid-air interface, \( \theta_W \) is the apparent contact angle and \( \theta \) is the contact angle for a smooth surface. Given the contrast of Sample 1 and Sample 2, they have the nearly same factor \( f \) but totally different apparent contact angle, which is because of the self-assembling due to PFOTES, which causes the surface energy of waste marble powder to decrease so that the angle \( \theta \) increases. However, the contact angle values from Sample 2 to Sample 11 differ little. They all have the same surface roughness values, the nearly same contact angle but totally different sliding angle values. This implies that with the increase of PFOTES’s concentration the wetting model must change from the Wenzel model to the Cassie-Baxter model. The schematic diagram below shows the conversion.

As shown in Fig. 7, with an increase of PFOTES’s concentration, the surface energy decreases so that the water droplets find it more and more difficult to penetrate the gaps. Thus, an air mat seemingly supports the water droplet. In this case, the water droplet on the surface is actually rolling as a sphere rather than sliding as a half-sphere, which has a much bigger contact area with the substrate. The former situation corresponds to the rolling friction and the latter one corresponds to the sliding friction. Therefore, the sliding angle values certainly vary greatly.

4.4 Robustness characterization

In this chapter, the robustness was measured. After the super-hydrophobic waste marble powder was bonded on the surface, a 120 mesh sand paper was covered on the coating and a 100 g weight acted as the constant pressure on the sand stone. After that, a sand paper was pulled at the speed of 3 cm/s. The scheme was shown in Fig. 8(a).

Sample 11 was investigated. Figure 8(b) displayed the contact angle and sliding angle values after every robustness test. As displayed in this figure, after 10 times’ robustness tests, the contact angle and sliding angle values changed slightly. The contact angle and sliding angle ranged from 147° to 155° and 6.8° to 8.5° respectively. The difference was inconspicuous. Therefore, the conclusion could be drawn that such kind of super-hydrophobic showed a good robustness and was able to be coated on the substrate firmly.

5. Conclusions

As a summary, the study described in this paper proposed a simple but effective self-assemble way to reuse waste marble powder to produce super-hydrophobic self-cleaning coating by self-assembling PFOTES on the particle surface. Conclusions can be made that a very low concentration (mass percentage 0.1208%) of PFOTES causes the water contact angle to change from 11.3° to 138°. Moreover, with an in-

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Fig. 6 The wetting models of super-hydrophobic (a): Wenzel model; (b): Cassie-Baxter model.

Fig. 7 The conversion of the wetting model with the increase of PFOTES’s concentration. ◯ original waste marble powder particle; ◆: modified particle.

Fig. 8 (a): The scheme for the robustness characterization; (b): The contact angle and sliding angle values after every test.
crease of PFOTES, the contact angle value increases slowly from 138° to 153°. However, the sliding angle value changes drastically varying from over 180° (the water droplet will not fall even it is turned upside down) to 6.8°. Thus, the water-wetting model would change from the Wenzel model to the Cassie-Baxter model. The reason is that the increasing PFOTES’ concentration decreases the surface energy and causes the gaps between particles to act more and more in a hydrophobic manner, thus increasingly preventing water permeation. Eventually, an air mat and the sliding angle, therefore, decrease effectively to support the water droplet. Therefore, when considering the properties of a self-cleaning material based on the application of a super-hydrophobic material, although the water contact angle is an important reference, it is still necessary to consider the factor of sliding angle as well. Furthermore, the super-hydrophobic waste marble powder coating displayed an excellent robustness. After 10 times’ robustness tests, the contact angle and sliding angle changed a little (ranged from 147° to 155° and 6.8° to 8.5° respectively). Therefore, if an appropriate adhesive was selected, the super-hydrophobic waste marble powder was capable of working for a long time.

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