

# Chopped carbon fiber reinforced CeO<sub>2</sub>/PMMA/PVDF superhydrophobic composite coating with enhanced abrasion durability

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**Abstract.** The practical applications of bioinspired superhydrophobic surfaces are often restricted by poor mechanical wear-resistance. CeO<sub>2</sub> nano particles toughened polymethyl methacrylate (PMMA)/polyvinylidene fluoride (PVDF) composite coating with water contact angle (WCA) of 152° and sliding angle (SA) of 5° was fabricated by drop casting method. After sand abrasion test, the WCA of the as-prepared CeO<sub>2</sub>/PMMA/PVDF superhydrophobic coating decreased to 103° and the SA increased to above 20°. To enhance the wear-resistance, chopped carbon fiber was used to reinforce the CeO<sub>2</sub>/PMMA/PVDF superhydrophobic composite coating. The results show that WCA of the chopped carbon fiber reinforced CeO<sub>2</sub>/PMMA/PVDF superhydrophobic composite coating was able to maintain above 140° after continuous sand abrasion. It indicates that the chopped carbon fiber is a very effective approach to improve wear-resistance of the CeO<sub>2</sub>/PMMA/PVDF superhydrophobic composite coating and has prosperous potentiality towards mechanical robust water repellent coating.

**Keywords:** superhydrophobic; ceria; carbon fiber; wear resistance.

## 1 Introduction

Owing to their unique applications in self-cleaning [1,2], anti-icing[3], drag-reduction [4] and many other fields, superhydrophobic surfaces have attracted considerable scientists to carry on researches. Usually, superhydrophobicity is defined as water contact angle (WCA) above 150° and sliding angle (SA) below 10° [5-8]. In general, nano/micro-hierarchical structures and low surface energy materials are believed to be the two critical factors to construct superhydrophobic surfaces [9]. Up to now, many methods have been dedicated to fabricate superhydrophobic surfaces, including sol-gel [10,11], chemical vapor deposition [12], phase separation [13] and electrochemical deposition [14]. Among these methods, nano and/or micro particles, such as SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and ZnO particles [15-17], are effective approaches to achieve superhydrophobicity when decorated with low surface energy materials. Some researches revealed cerium dioxide exhibits hydrophobicity as a result of the micro-

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molecule alkane absorbed on the surface, which provides a new choice to prepare superhydrophobic surfaces [18]. Liu et al [19]. developed a ceria superhydrophobic surface on MB8 aluminum plate adopting electrochemical deposition with the raw materials  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and myristic acid. However, this approach is much more complicated than composite coating method to fabricate superhydrophobic surfaces and is not feasible to apply on polymer composite surface.

Wear-resistance has always been a big challenge to the practical applications of the superhydrophobic surfaces. Carbon fiber possesses high strength, modulus as widely used reinforcement for composite materials, which is supposed to improve the wear-resistance of superhydrophobic surfaces[20,21]. It is well-known that polyvinylidene fluoride (PVDF) plays a pivotal role in fabricating microfiltration and ultrafiltration membranes because of its outstanding properties of wear-resistance, thermal stability and corrosion-resistance. However, PVDF tends to crystallize when preparing membranes with it alone, which leads to pinholes on the surfaces. Furthermore, if the curvature of the coatings is too low or the surface indents, unsticking with the substrate can be easily observed [22, 23]. Considering the eminent intermiscibility with PVDF and good adhesion with substrates, polymethylmethacrylate (PMMA) is frequently used to modify PVDF[24], which offer a good resin to prepare superhydrophobic surfaces.

Herein, we report our work in fabricating a superhydrophobic composite coating from  $\text{CeO}_2$ /PMMA/PVDF by drop casting method that is easy to apply on large scale surfaces including polymer composite material surfaces. Furthermore, a certain amount of chopped carbon fibers with different length were added to improve the wear-resistance as well as retain its superhydrophobicity. According to our work, chopped carbon fibers can greatly improve wear-resistance of the composite coating, which paves the way for the large-scale industrial application of this superhydrophobic coating.

## 2 Materials and methods

### 2.1 Materials

Commercial PVDF powders with number-average molecular weight of 100000 g/mol were purchased from Slovey Co. Ltd. (American). PMMA powders were provided by Chimei Co. Ltd. (Taiwan).  $\text{CeO}_2$  particles with average diameter of 1 $\mu\text{m}$  were offered by GanzhouGuangli Co. Ltd. (China). T700 carbon fibers were supplied by Toray Co. Ltd. (Japan). Chopped carbon fibers with the special length of 1mm, 3mm and 5mm were made by cutting the T700 carbon fibers. Dimethyl formamide (DMF) and absolute alcohol were bought from Huadong Reagent Factory, Shenzhen, China.

### 2.2 Preparation of the superhydrophobic composite coating

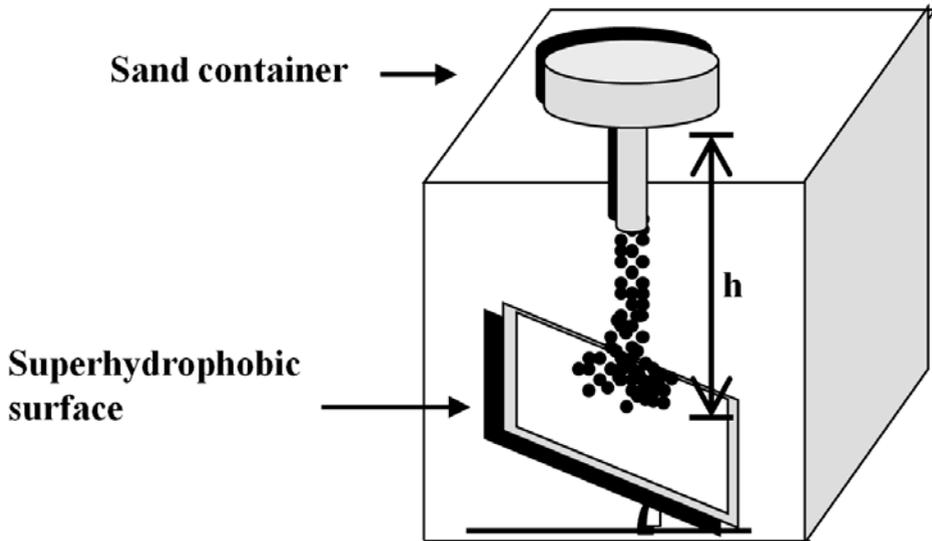
The glass fiber reinforced epoxy resin composite plates (100mm x 100mm x 1mm) were fabricated by vacuum assistant resin infusion process (VARI). The substrate was polished with 600 mesh sand papers in one direction, and then ultrasonically washed in absolute alcohol for 10 min.

The preparation of the superhydrophobic composite coating mainly includes the following steps: Firstly, 0.75 g PVDF powders and 0.5 g PMMA powders were dispersed in 6 g DMF to form a uniform solution by magnetic stirring at 70 °C. Then, 2.75 g  $\text{CeO}_2$  particles were added into the above solution and dispersed by magnetic stirring. After this, the solution was smeared on the as-treated composite plate by drop casting method. In order to evaporate the solvent, the substrate was placed in ambient temperature for 4 h. Finally, a substrate with superhydrophobic surface can be obtained by curing at 100 °C for 45 min. Similarly, as for coatings with the chopped carbon fibers, carbon fibers were added in the solution simultaneously with  $\text{CeO}_2$  particles. Subsequently, magnetic stirring was utilized to produce a uniform solution. Then, dip the solution on the as-treated composite plate. The following steps were the same as above coating process.

## 2.3 Characterization

The WCA and SA values of the composite coating were measured by a Contact Angle Meter (SL-200B, Shanghai Suolun Co. Ltd.) with a droplet of distilled water. The WCA values are the average values of 5 measurements on different areas of the test composite coating at the room temperature with the distilled water of 5  $\mu\text{L}$ . The measurement of SA values was acquired by dropping a 10  $\mu\text{L}$  water droplet from about 4 mm height above the composite coating surface. SA values were also measured at 5 different areas. The morphology of the composite coating was obtained by the scanning electron microscopy (SEM) (Quanta-200, FEI Co. Ltd.).

The hardness of the composite coating was evaluated according to GB6378-86 criterion via a pencil hardness tester. The wear-resistant property of the coating was estimated by impacting the coating with silica sands according to the method shown in the literature[25]. Fig. 1 shows the schematic of the abrasion test. The average diameter of the silica sand is 1mm with the flow rate of 0.6 L/min. While the slant angle of the surface is 45°, the distance between sand container and superhydrophobic surface (h) is fixed as 45 cm. After impacting the coatings for 30s, WCA and SA values of the surface were measured.



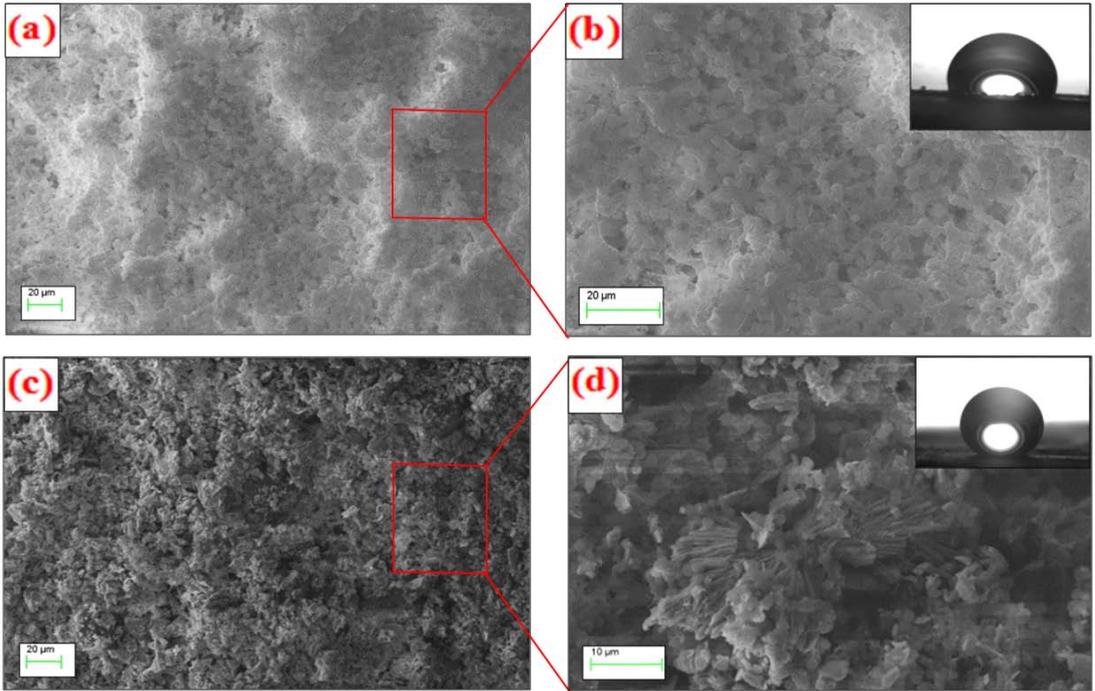
**Figure 1.** Schematic of the sand abrasion test method

## 3 Results and discussion

### 3.1 Superhydrophobicity of the $\text{CeO}_2/\text{PMMA}/\text{PVDF}$ composite coating

Nano-micro structure plays a decisive role in determining the superhydrophobic property of a coating surface. Fig. 2 shows the micro-scale structures of PMMA/PVDF and  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  coating. From the SEM image of the PMMA/PVDF coating (Fig. 2(a) and 2(b)), it could be seen that the surface is relatively smooth without forming a heterogeneous structure. So the PMMA/PVDF coating only reveals the hydrophobic property with the WCA value 114° and the SA value larger than 20°. As to the  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  composite coating (Fig. 2(c) and 2(d)), a heterogeneous structure can be observed and shows a high porous structure on the surface. Also, a micro size flower-like structure that owes a nano size lamellar structure on the top can be found, as shown in Fig. 2(d), which forms an excellent nano-micro hierarchical structure. And due to the nano-micro hierarchical structure

the  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  composite coating surface reveals the superhydrophobic property. The WCA value and the SA value are  $152^\circ$  and  $5^\circ$ , respectively.

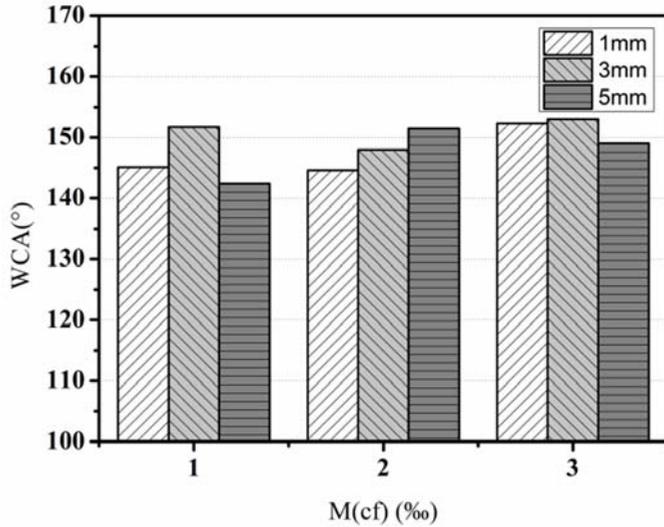


**Figure 2.** The SEM images of the composite coating: (a, b) PMMA/PVDF, (c, d)  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$

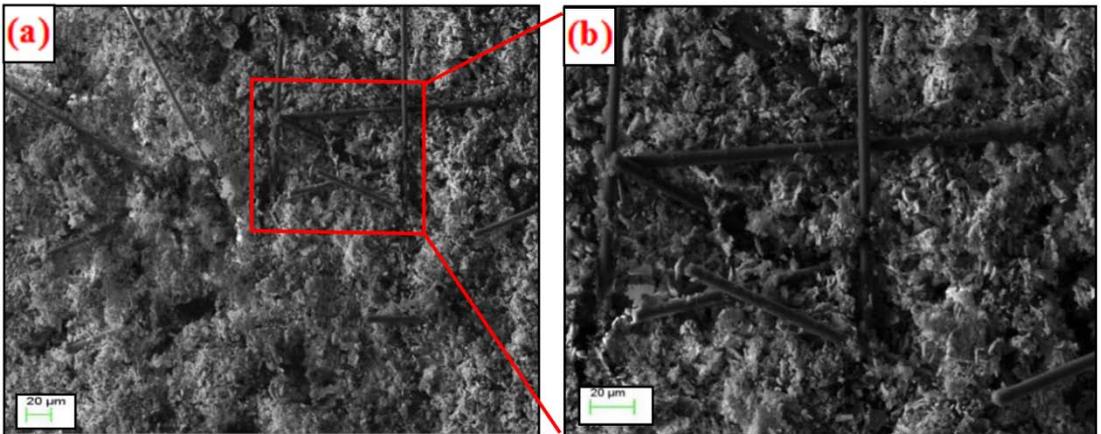
### 3.2 Superhydrophobicity of chopped carbon fiber reinforced $\text{CeO}_2/\text{PMMA}/\text{PVDF}$ composite coating

On the basis of the above  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  composite coating, different quantities of T700 chopped carbon fibers (1mm, 3mm and 5mm) were added to reinforce the composite system. Like the above composite coating, the  $\text{CeO}_2$  particles occupy 27.5 wt %, the solvent takes up 65 wt % and the mass ratio between PVDF and PMMA is 6:4 in the modified composite coating.

Fig. 3 presents the WCA values of different composite coatings after adding a certain amount of chopped carbon fibers with the particular length. It reveals that the length and quantity of the chopped carbon fibers have little influence on the hydrophobicity of the composite coatings. All the WCA values of these composite coatings are above  $140^\circ$  and some of them are above  $150^\circ$ , which shows small amount of chopped carbon fibers has no effect on the hydrophobicity of  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  coating.



**Figure 3.** The WCA values of the modified composite coating surfaces with different quantities and length of the chopped carbon fibers

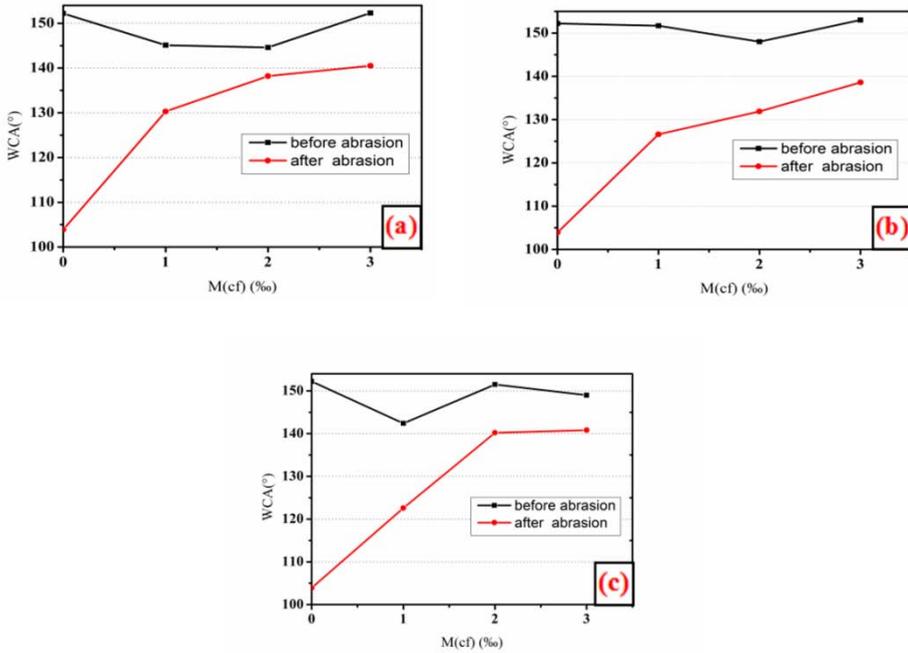


**Figure 4.** SEM images of carbon fiber reinforced  $\text{CeO}_2$ /PMMA/PVDF coating

From the SEM images of the reinforced  $\text{CeO}_2$ /PMMA/PVDF composite coating, which was added in 2 wt% chopped carbon fibers with the length of 3 mm (Fig. 4), it could be seen that there are many chopped carbon fibers distributed on the surface, and these fibers crisscross each other, which forms a stereoscopic structure. Besides, the porosity and embossment structure can be easily found. And this modified composite coating exhibits superhydrophobicity with a WCA value up to  $153^\circ$  and the SA value of  $5^\circ$ , which means chopped carbon fiber doesn't affect its superhydrophobicity.

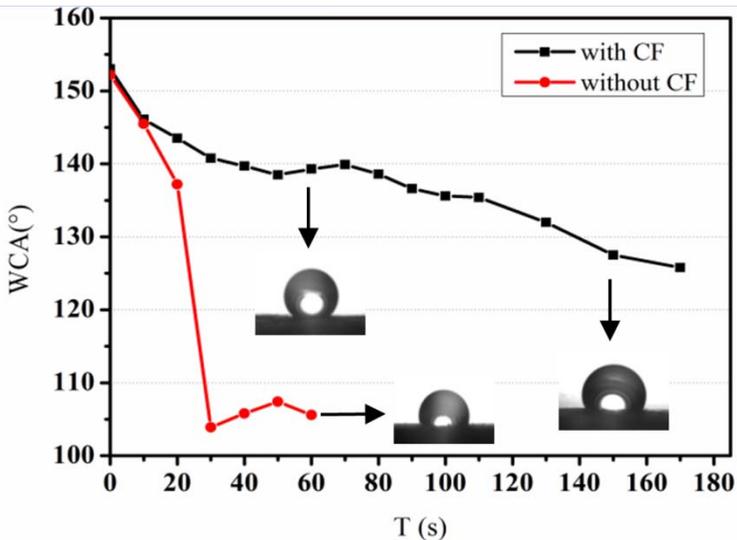
### 3.3 Wear-resistance of the prepared coatings

The wear-resistance of the chopped carbon fiber reinforced  $\text{CeO}_2$ /PMMA/PVDF superhydrophobic composite coating was evaluated and compared with the unmodified  $\text{CeO}_2$ /PMMA/PVDF composite coating (Fig. 5).



**Figure 5.** The hydrophobicity of WCA values of chopped carbon fiber reinforced CeO<sub>2</sub>/PMMA/PVDF coating before and after the abrasion test: (a) 1mm, (b) 3mm, (c) 5mm

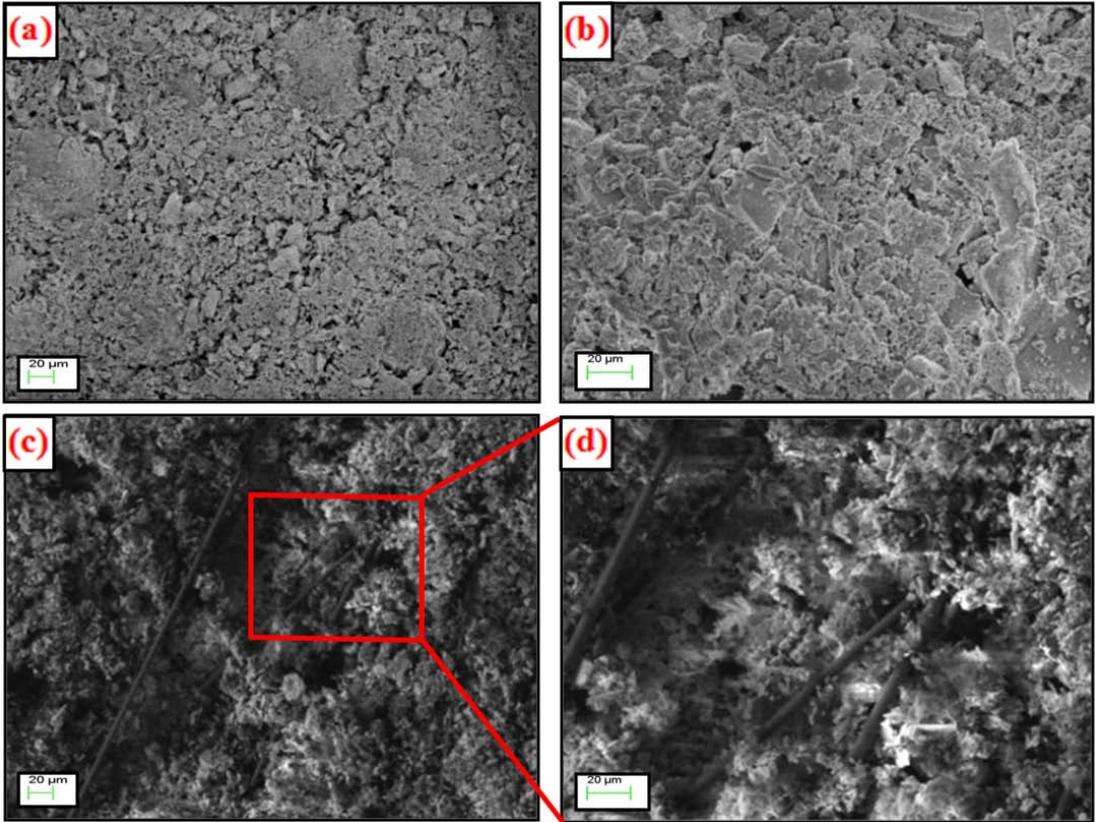
Fig. 5 shows that the wear-resistance of the composite coating is improved after the chopped carbon fibers were added. Furthermore, the wear-resistance increases with the amount of carbon fibers. Usage of 3 wt% 5 mm chopped carbon fibers is able to keep the WCA above 140.8° after the abrasion test, while WCA of the composite coating without chopped carbon fibers decreases from 152° to 104°.



**Figure 6.** Effect of sand abrasion on the WCA of the unmodified and modified composite coating

Effect of sand abrasion on the WCA of the unmodified and modified composite coating is shown in Fig. 6. The modified composite coating is the one which was reinforced by 3 wt% 3 mm chopped carbon fiber. From Fig. 6, it can be found that the WCA value of the unmodified composite coating has a striking sink in the first 30s, especially a decrease from 137° to 103° can be observed from 20s to 30s. However, for the composite coating reinforced with the chopped carbon fibers, the WCA value

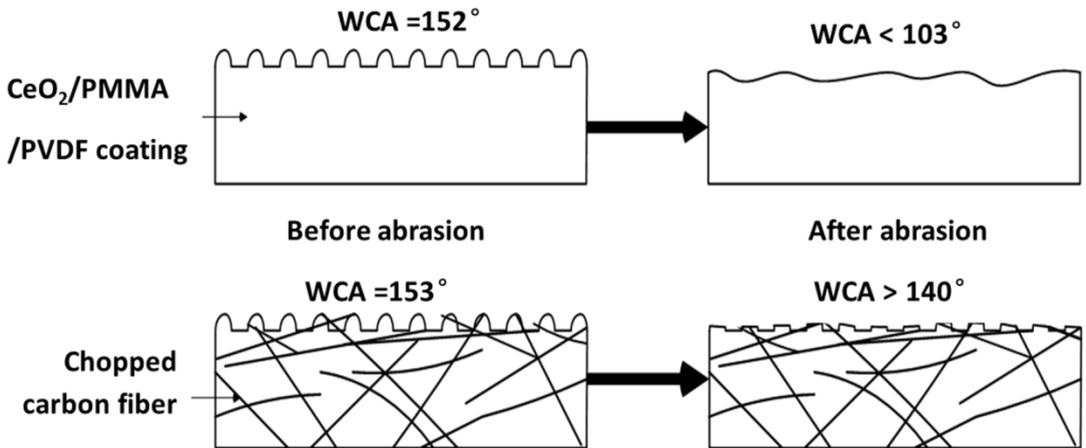
just falls from 153° to 140° in the first 30s and is sustained by a plateau around 140° in the following 50s. Then the value descends mildly until all the coating is abraded completely. Therefore, it can be concluded that the chopped carbon fibers can prevent the composite coatings from being abraded dramatically, which can protect the rough structure on the surface as well as its hydrophobicity.



**Figure 7.** SEM images of (a, b)  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  coating after abrasion, (c, d) chopped carbon fiber reinforced  $\text{CeO}_2/\text{PMMA}/\text{PVDF}$  coating after abrasion

Fig. 7(a) and 7(b) are the SEM images of the coating without carbon fibers after abrasion. The abrasion traces of the silica sands can be seen on the surface and as a result the surface morphology changes from rough to flat. Simultaneously the porosity and embossment structures are destroyed by the silica sands. So the WCA value experiences a dramatic decline. On the contrary, even though some fibers were exhibited on the surface after abrasion, the modified composite coating still shows a rough structure (Fig. 7(c) and 7(d)), which is the pivot of the hydrophobicity.

Several reasons contribute to improve the wear-resistance of the chopped carbon fibers reinforced coatings. First, T700 carbon fibers with excellent modulus and strength are able to improve the mechanical property of the coating. Secondly, the self-lubrication property of carbon fibers helps to protect coating surface from sand abrasion. Thirdly, fibers in the coating crisscross each other and form a stereoscopic structure (Fig. 4 and 8), which can prevent the surface from further abrasion. Finally, thanks to the reinforcement effect of carbon fibers, the hardness of the coating increase from 4H to 5B (hardness test method as in reference [26]), which also contribute to improve the wear resistance of carbon fiber reinforced coating.



**Figure 8.** Schematic of the chopped carbon fiber to improve the wear-resistance

## 4 Conclusions

In this work, CeO<sub>2</sub>/PMMA/PVDF composite coating with superhydrophobicity was successfully prepared by drop casting method. The CeO<sub>2</sub>/PMMA/PVDF composite coating showed a WCA value of 152° and a SA value of 5°. Chopped carbon fibers were used to enhance the wear resistance of CeO<sub>2</sub>/PMMA/PVDF composite coating without affecting its superhydrophobicity, which retains WCA of 153° and SA of 5°. Sand abrasion would cause the WCA of CeO<sub>2</sub>/PMMA/PVDF coating decrease from 152° to 103°. It is demonstrated in this work that a small amount of chopped carbon fibers is able to improve the wear-resistance of CeO<sub>2</sub>/PMMA/PVDF coating dramatically without affecting the coating process. 3 wt% of 3 mm chopped carbon fibers improves the WCA by approximately 40° (from 103° to above 140°). Carbon fibers with excellent mechanical properties and self-lubricant property are capable of improving the wear-resistance of the CeO<sub>2</sub>/PMMA/PVDF composite coating effectively, which is expected to be a prosperous approach leading to mechanical robust superhydrophobic coating.

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