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Facile fabrication of superhydrophobic conductive graphite nanoplatelet/vapor-grown carbon fiber/polypropylene composite coatings

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ABSTRACT

The fabrication of superhydrophobic surfaces with mechanical durability is challenging because the surface microstructure is easily damaged. Herein, we report superhydrophobic conductive graphite nanoplatelet (GNP)/vapor-grown carbon fiber (VGCF)/polypropylene (PP) composite coatings with mechanical durability by a hot-pressing method. The as-prepared GNP/VGCF/PP composite coatings showed water contact angle (WCA) above 150° and sliding angle (SA) less than 5°. The superhydrophobicity was improved with the increase of VGCF content in the hybrid GNP and VGCF fillers. The more VGCFs added in the GNP/VGCF/PP composite coating, the higher porosity on the surface was formed. Compared to the GNP/PP and VGCF/PP composite coatings, the GNP and VGCF hybrid fillers exhibited more remarkable synergistic effect on the electrical conductivity of the GNP/VGCF/PP composite coatings. The GNP/VGCF/PP composite coating with GNP:VGCF = 2:1 possessed a sheet resistance of 1 Ω/sq. After abrasion test, the rough microstructure of the GNP/VGCF/PP (2:1) composite coating was mostly restored and the composite coating retained superhydrophobicity, but not for the VGCF/PP composite coating. When the superhydrophobic surface is mechanically damaged with a loss of superhydrophobicity, it can be easily repaired by a simple way with adhesive tapes. Moreover, the oil-fouled composite surface can regenerate superhydrophobicity by wetting the surface with alcohol and subsequently burning off alcohol.

1. Introduction

Superhydrophobicity is defined as water contact angle (WCA) above 150° and sliding angle (SA) below 10° [1–3]. The chemical composition of the material and the microstructure (i.e., micro and nanoscale roughness) play key roles for the formation of superhydrophobic surfaces [4–6]. In general, superhydrophobic surfaces are produced mainly in two ways [7]. One is to create a rough structure on a hydrophobic surface, which possesses a WCA lager than 90°, and the other is to modify rough surface by low-surface-energy material.

Over the past decades, application of superhydrophobic surfaces has attracted considerable interests in many fields, such as self-cleaning, anti-corrosion, anti-adhesion, and oil-water separation [8–10]. When combined with electrical conductivity, superhydrophobic surfaces can be used in electromagnetic interference and shielding materials due to their capability to remove static charges accumulated on the surfaces [11–13]. In recent years superhydrophobic surfaces have been prepared using carbonaceous materials, including amorphous carbon [14–16], carbon nanotubes [3,16,17], graphene [4] and Ketjen black [8,18]. Up to now, many methods have been used to prepare superhydrophobic surfaces [10,19–26], such as biologically inspired approaches, electrospinning, phase separation, crystal growth, templating, etching, physical or chemical vapor deposition, electrochemical reaction and deposition, sol–gel processing and self-assembly. In particular, the hot-pressing method is a simple way used to obtain superhydrophobic surfaces. Zhu et al. [27] fabricated a mechanically robust superhydrophobic metal/polymer composite surface by a hot-pressing approach. For engineering applications, to improve mechanical resistance of artificial superhydrophobic surfaces is critical. Xu et al. [28] described a simple and inexpensive lamination templating method to create superhydrophobic polymer surfaces with excellent abrasion resistance. Cui et al. [29]

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prepared highly durable superhydrophobic surface with multi-scale structures by dip-coating process on epoxy paint surface.

Both graphite nanoplatelet (GNP) and vapor-grown carbon fiber (VGCF) possess high electrical conductivity [30–32]. The WCA for flat graphite is about 85° [3]. However, the use of hybrid GNP and VGCF fillers has not been reported in the preparation of superhydrophobic surfaces until now.

Herein, we report superhydrophobic conductive GNP/VGCF/PP composite coatings prepared by a hot-pressing method for the first time. The GNP/PP and VGCF/PP composite coatings were also prepared for comparison. All of the as-prepared composite coatings possess high electrical conductivity. The GNP/VGCF/PP composite coating has WCA values larger than 150° and SA values less than 10°. The GNP/VGCF/PP composite coating not only displays a synergetic conductive effect but also an improved mechanical stability as the hybrid VGCFs provide conductive network with more rapid paths and the GNPs protect VGCFs from mechanical damage to some extent (Fig. 1). Moreover, it is easy to regenerate the superhydrophobicity of GNP/VGCF/PP composite coating with adhesive tapes and by burning off alcohol to solve oil contamination problem.

2. Experimental

2.1. Materials

GNPs with a diameter of 1–20 μm and a thickness of 5–15 nm were provided by Xiamen Knano Graphene Technology Co., Ltd. VGCFs with a diameter of 100–500 nm and an aspect ratio from 10 to 500 were supplied by Taiwan Unitetekin International Co., Ltd. PP (1320HX) was purchased from BASF Co., Germany. The adhesive tape, print paper and (PET) film were commercially available. All of the materials were used as received.

2.2. Preparation of superhydrophobic conductive GNP/VGCF/PP composite coatings

With a total mass of 0.05g, GNPs and VGCFs were added in ethanol (200 mL) at different GNP:VGCF mass ratios of 8:1, 4:1and 2:1, respectively. Hybrid GNP and VGCF fillers were prepared by stirring the mixture for 4 h followed by a drying process. The hot-pressing process used to fabricate the superhydrophobic GNP/VGCF/PP composite coatings is schematically presented in Fig. 2. Firstly, a PP plate was prepared in a stainless mold with a diameter of 50 mm and a thickness of 3 mm. Then the powders of hybrid filler were distributed in the same mold. At last, the PP plate was covered on the hybrid fillers followed by a hot-pressing process under a pressure of 12 MPa at 180 °C with different infiltration times. After demolding, the composite coating was treated with adhesive tape for 7 times and then immersed in water to remove the unbound powders. When using a low hybrid filler loading, the PP melt would infiltrate onto the composite coating surface and form PP film (as shown in Fig. 3), leading to a decrease of the superhydrophobicity. Therefore, the hybrid fillers with a mass of 0.05 g were chosen to prepare the superhydrophobic composite coatings. For comparison, the GNP/PP and VGCF/PP composite coatings were also prepared with the same method.

2.3. Characterization

The WCA and SA values were measured by a DATA Physics OCA20 contact angle analyzer (Germany) at room temperature. Water droplets with a volume of 4 μL were used to measure the WCA values. The measurement of SA values was carried out by dropping a 10 μL water droplet from about 4 mm height above the composite coating surfaces. Both WCA and SA values were measured at more than five different positions for each sample. Field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) was operated at 3 kV to observe the surface morphologies of superhydrophobic conductive composite coatings. Sheet resistances (an important evaluation criterion for the electrical conductivity) were measured by standard four-probe technique using a RTS-4 four-probe conductivity meter from Guangzhou 4 Probes Tech., China. The optical images were recorded by a Canon 500D digital camera.

3. Results and discussion

3.1. Superhydrophobicity and conductivity

Fig. 4 presents WCAs for different filler compositions with various infiltration times, showing that WCAs increase with increasing VGCF content and reach a maximum value at the infiltration time of 60 min. Without VGCF, the WCA values of GNP/polymer composite coatings are about 130°, revealing the GNP/polymer composite coatings possess only hydrophobicity but not superhydrophobicity. Hybrid GNP and VGCF fillers, even VGCF at low content (GNP:VGCF = 8:1), can endow the composite coatings superhydrophobicity. The infiltration time has little influence on the WCA values of composite coatings, but long infiltration time results in polymer melts penetrating onto the surfaces of composite coatings, causing loss in superhydrophobicity [3].

Fig. 5 shows the behaviors of water droplet depositing on the GNP/VGCF/PP (8:1) composite coating and water jet bouncing off the surface. Keeping spherical shapes, water droplets depositing on the composite coating with a diameter of 25 mm clearly shows superhydrophobic behavior of the GNP/VGCF/PP composite coating (Fig. 5a). When a water jet was conducted on the composite coating, the water jet bounced off the coating and changed into a string of water droplets, indicating an excellent water repellency property (Fig. 5b). There was no trace left on the composite coating after the water jet bouncing off (Fig. 5c). The position where the water droplets contact with the composite coating are bright (mirror-like phenomenon) because of the reflection of light from

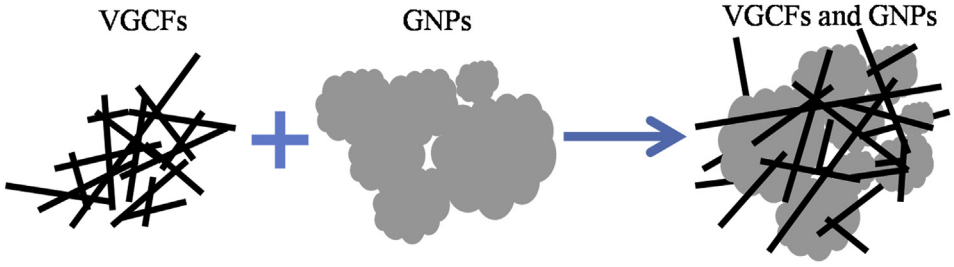

Fig. 1. Schematic illustration of the synergetic conductive effect and improved mechanical stability. VGCFs provide conductive network with more rapid paths while the GNPs protect VGCFs from mechanical damage to some extent due to the relatively large contact area of platelet.