Journal of Colloid and Interface Science 436 (2014) 111–121

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Facile synthesis of nano cauliflower and nano broccoli like hierarchical superhydrophobic composite coating using PVDF/carbon soot particles via gelation technique

Bichitra Nanda Sahoo, Kandasubramanian Balasubramanian *

Department of Materials Engineering, Defence Institute of Advanced Technology (DIAT), Girinagar, Pune 411025, India

ARTICLE INFO

Article history:
Received 16 May 2014
Accepted 17 August 2014
Available online 1 September 2014

Keywords:
Superhydrophobic
Camphor soot particle
Candle soot particles
Broccoli
Crystallization
Fibrils

ABSTRACT

We have elucidated a cost effective fabrication technique to produce superhydrophobic polyvinylidene fluoride (PVDF/DMF/candle soot particle and PVDF/DMF/camphor soot particle composite) porous materials. The water repellent dry composite was formed by the interaction of non-solvent (methanol) into PVDF/carbon soot particles suspension in N,N-dimethylformamide (DMF). It is seen that longer quenching time effectively changes the surface morphology of dry composites. The nano broccoli like hierarchical microstructure with micro or nano scaled roughen surface was obtained for PVDF/DMF/camphor soot particle, which reveals water contact angle of 172° with roll off angle of 2°. However, composite coating of PVDF/DMF/candle soot particle shows nano cauliflower like hierarchical, which illustrates water contact angle of 169° with roll off angle of 3°. To elucidate the enhancement of water repellent property of PVDF composites, we further divulge the evolution mechanism of nano cauliflower and nano broccoli structure. In order to evaluate the water contact angle of PVDF composites, surface diffusion of water inside the pores is investigated. Furthermore, the addition of small amount of carbon soot particles in composite not only provides the crystallization of PVDF, but also leads to dramatical amendment of surface morphology which increases the surface texture and roughness for superhydrophobicity.

1. Introduction

Superhydrophobic/self cleaning surfaces, those reveal contact angle (CA) with more than 150° and sliding angle (SA) less than 5°, are of high scientific and industrial interest [1–3]. These interests are not only encouraged by the super water repellency property confirmed by natural leaves (lotus, rice, taro, rose, etc.) [4,5], but also some natural species such as butterfly wings [6], mosquito eyes [7], and water strider legs [8] have brought scientific importance to surface. Since the key elements of surfaces are chemical composition and micro-nano-hierarchical texture, it thus promotes superhydrophobic states of the surface. Hence, various artificial superhydrophobic materials have been aroused, which brings scientific potential effort for use in industrial applications. In particular, large efforts have been explored to create artificial "lotus effect" materials which imitate the properties and characteristics of natural water repellency systems [8,9]. It is also reported that these imitates usually comprised of low-surface-energy and high roughened surface [10,11]. Earlier, various scientific reported have divulged details significantly to achieve superhydrophobic surface, since it is not possible to attain self cleaning property without using low surface energy with suitable roughed surfaces [12]. Hence, combination of micro hierarchical with nano-hierarchical morphological structure and some other effective techniques have been used to tailor superhydrophobicity.

Design and fabrication of surface-rough (e.g., cully-flower-like, rose petal etc) spherical structure have attracted much attention because of their special structure and wide applications in snow adhesion to glass, anti-corrosion, anti-fouling and especially in constructing superhydrophobic coatings (films) by mimicking the lotus leaf surface structure with dual-size roughness [13,14]. Earlier, a few reports have been discussed on the fabrication of polymer microspheres such as polystyrene–polymethyl methacrylate, polylactide, and poly (lactide-co-glycolide) [15,16]. Among all the existing polymers, fluorinated polymers have low surface energy hence; these can be used to fabricate superhydrophobic coating with enhanced surface roughness [17]. It is suggested that fluorinated polymer such as polyvinylidene fluoride with porous structure is used to achieve to superhydrophobicity with contact angle of more than 155° [14].

* Corresponding author.
E-mail address: meetkbs@gmail.com (K. Balasubramanian).

http://dx.doi.org/10.1016/j.jcis.2014.08.031
0021-9797/

On the other hand, it is found that carbon based fluorine polymer composite is highly hydrophobic. From the viewpoint of potential applications of PVDF/carbon superhydrophobic composite coatings (e.g., paints, cloth, glass, and interior fabrics), it has been considered as important property, but it is difficult to design super hydrophobic coating with different textured surface with retained superhydrophobic [18]. However, our recent publication has reported the effect of graphite content in EPF (expanded polystyrene foam) and the PVDF composite, which exhibited maximum water contact angles of 129° and 138° for EPF and PVDF composites, respectively [19,20]. The surface texture reveals the variation of surface roughness, which enables anisotropic surface wettability. The present work exhibits a promising approach for fabricating a nano flake forest in polymer structures for various industrial applications. Balasubramanian et al. have revealed anti-corrosive coating system-based waste thermoplastic materials containing camphor soot particles to impart good UV resistance and water repellency at ambient temperature [21]. Literature also reports the cost effective fabrication EPF/graphite composite for superhydrophobic application using spraying technique [22]. So far graphene materials is considered as a single atom – thick sheet composed of sp2 hybridized carbon atom which shows hydrophobicity [23]. It is observed that recently graphene–polymer composites also gain escalating notice in recent years [24–28] because they acquire enhanced properties such as thermal conductivity [29], electrical conductivity [30] and stimulation responsive properties [28]. A few reports have demonstrated the wetting characteristics of the surface functionalized graphene-polymer composite surface [31,32]. Furthermore, it is known that the creation of surface roughness, especially hierarchically micro/nano-scaled microstructures, may progress the water repellency and anti-bio fouling property of materials. The available techniques such as lithographic, spray coating, spin coating and templating have been extensively explored to fabricate microsphere like structure to bring superhydrophobicity. Although, these techniques are used to fabricate hydrophobic surface, it requires surface treatment with low surface energy materials such as silane materials. Hence, with this insight, we developed gelation technique which has brought special attention to fabricate microsphere with roughed surface without any surface treatment. Recently, use of the combination of phase inversion process and gelation technique for fabrication of PVDF based superhydrophobic composite coating has brought special attention to material scientist. Hence, these techniques are comprehensively used to fabricate microspheres with macromolecular spherulites on the composite surface which enhance the surface roughness to tailor superhydrophobic property. Fabrication of macromolecular aggregates with spherulites in PVDF composite is an important surface morphology, which is strongly influenced by types of solvents (poor or good solvent) and drying conditions (temperature) [33,34]. So it is reasonable to fabricate PVDF/carbon materials composite coating exhibiting superhydrophobicity using gelation technique.

Here, in this paper we have demonstrated a feasible method to produce superhydrophobic PVDF/camphor soot particle and PVDF/candle soot particle composite using combination of solvent exchange and slow gelation process with improved surface roughness. In the present study, a simple and effective route for extraction of carbon soot particles from the combustion of camphor and candle has been adopted. So far, a few literatures have been acknowledged the details of superhydrophobicity of PVDF/carbon composite. For first time superhydrophobicity of camphor soot and candle soot particles was revealed by Sahoo et al. [35,36]. Since, the obtained carbon soot particles are highly hydrophobic in nature; we have explored phase inversion process and slow gelation technique for fabrication of PVDF/camphor soot and PVDF/candle soot composite coating for first time. The solution of PVDF/camphor soot and PVDF/candle soot (camphor soot and candle soot of 1 wt% with respect to PVDF) in DMF was changed to a gel by absorbing a nonsolvent (methanol). After solvent replacement and drying, porous PVDF/camphor soot and PVDF/candle soot materials were obtained. Furthermore, the conversion of Wenzel state to Cassie state is proposed to tailor the energetically favorable of superhydrophobicity of PVDF composite surfaces. The evolution of surface morphology is investigated by FESEM (Field emission scanning electron microscopy), and DSC (differential scanning calorimetry). The surface wettability was measured by the measurement of water contact angle. The interaction between the polymer and additives was investigated by Raman spectroscopy and XRD (X-ray diffraction). An attempt has been also made to demonstrate a comparison study of surface morphology of PVDF/DMF, PVDF/camphor soot and PVDF/candle soot composites.

2. Experimental section

2.1. Materials

PVDF with M_w of 2,75,000 was received from Sigma Aldrich, India. Methanol (99%, Alfa Aesor), N,N-Dimethylformamide (ACS, 99.8+%, Alfa Aesor), Acetone (99.8%, Sigma Aldrich), Ethanol (99.9%, Sigma Aldrich), were all used as received. Camphor tablet of size of (7 × 5 mm) ($C_{10}H_{16}O$, 96%, Sigma–Aldrich) was used as source for carbon soot particles without any further purification. Similarly, candle of size of (15 × 2 cm ($L \times D$)) was used as precursor for collecting carbon soot particles. Glass substrates (75″ × 25″ × 3″ mm) were received from Fisher Scientific (India). Water was supplied by a Barnstead Nanopure Water System (18.3 M^3 cm).

2.2. Cleaning of glass substrates

Glass substrates were carried out for ultrasonication (Sonicator Model-EI-6LH-SP, Sl. No-1209-122, India) at 20 kHz and 20 W in 100 ml ethanol for 25 min followed by ultrasonication using deionised water for 20 min. These cleaned glass substrates were then ready for using the collection of soot particles.

2.3. Generation of soot particles

A single camphor tablet (7 × 5 mm ($d \times t$)) was placed in a silica crucible and the entire assembly was kept inside a perforated polycarbonate chamber (PC). The camphor soot particles were collected on a glass substrate placed 50 mm above the flame. The schematic for collection of soot particles is illustrated in Fig. 1. It is observed that in the specific time duration, the emitted soot particles are coated in a layered pattern on the glass substrate. The collected

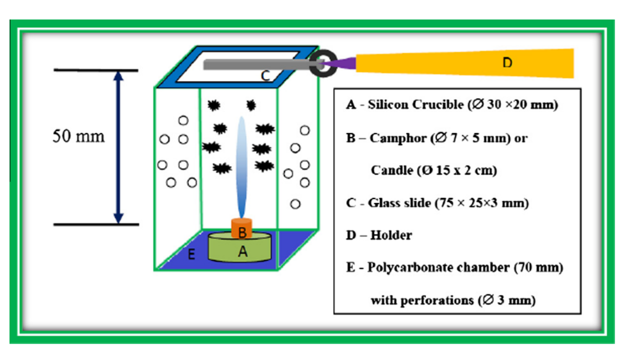

Fig. 1. Schematics for collection of soot particles of combustion of camphor and candle.