Hindawi Publishing Corporation
Journal of Polymers
Volume 2013, Article ID 615045, 4 pages
http://dx.doi.org/10.1155/2013/615045

Research Article

Effect of TiO_2 Powder on the Surface Morphology of Micro/Nanoporous Structured Hydrophobic Fluoropolymer Based Composite Material

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Received 26 March 2013; Accepted 5 June 2013

Academic Editor: Cornelia Vasile

The present work reports a simple and effective way to produce hydrophobic foams with polyvinylidene fluoride (PVDF) and TiO_2 by using a phase separation technique. This method involved the phase separation during the deposition of PVDF from its DMF solution with nonsolvent water in the presence of TiO_2. The surface morphology of hydrophobic surfaces was characterized by Field Emission Scanning Electron Microscope (FESEM). The maximum water contact angle of 129° was observed. The results confirm that the surface texture of polymer composite exhibits mixture of microporous and nanoporous structure. The impact of TiO_2 on the wettability property of polymer composite has been studied. The proposed methodology might find applications in the preparation of hydrophobic surfaces for industrial applications.

1. Introduction

The excellent water repellent surface is exhibited by the leaves of the lotus flower. These leaves are superhydrophobic; that is, water drops roll over, taking any impurities with it. The combination of surface roughness and water-repellent wax crystals gives superhydrophobic property. The fabrication of a superhydrophobic surface depends on the surface roughness and surface energy of materials [1]. Many artificial methods have been developed to fabricate superhydrophobic surfaces using techniques such as electrodeposition, plasma etching, laser treatment, sol-gel method, and solution immersion method. Phase separation method is an important technique for development of super hydrophobic surfaces [2, 3]. In this method, the product should be separated into a different phase from everything else that is present in the final reaction mixture. The phase separation method is the simplest method compared to the other methods mentioned above and the ease in forming large area and strong superhydrophobic coatings [4].

The process of harnessing and converting ambient energy sources into usable electrical energy is called energy harvesting. Piezoelectric materials can be used to harvest energy since they have the unique ability of converting mechanical strain energy into useful electrical energy [5]. Polyvinylidene fluoride (PVDF) is a piezoelectric polymer which exhibits hydrophobicity and can be employed in energy harvesting applications like sensors and actuators [6]. Compared to strain gauges, piezoelectric sensors offer superior signal-to-noise ratio and better high-frequency noise rejection. Piezoelectric sensors are, therefore, quite suitable for applications that involve measuring low strain levels [7]. They are compact and easy to embed and require moderate signal conditioning circuitry. These sensors are electromechanical systems that react to compression, and the sensing elements show almost zero deflection. This is the reason why piezoelectric sensors are so rugged and have an extremely high natural frequency and an excellent linearity over a wide amplitude range [8]. In recent years, the incorporation of inorganic additives into polymeric materials has expanded markedly for filtration

and gas separation membranes. As noted before, a variety of nanoparticles such as SiO_2, Al_2O_3, Fe_3O_4, ZrO_2, and TiO_2 have been introduced to modify organic membranes. Among them, TiO_2 has received the most attention because of its good physical and chemical properties, availability as well as its potential antifouling abilities [9–12].

In the present work, we continually focus on the fabrication of hydrophobic composite surface using TiO_2 and PVDF by the phase separation method. The effect of concentration of titanium dioxide on the water contact angle of porous structure of PVDF and surface morphology has been investigated.

2. Materials and Methods

2.1. Fabrication of PVDF/TiO_2 Composite. PVDF (molecular weight 2,80,000 g/mol), (N,N-dimethylformamide) DMF (99.8%), and acetone (99.8%) were received from Sigma Aldrich, and titanium dioxide powder (anatase) was purchased from Alfa Aesar. All the reagents were of analytical grade and used as purchased without further purification. Deionized water is used as nonsolvent. Prior to coating glass slides are cleaned with ethanol and then rinsed with deionized (DI) water and acetone, respectively, and dried in the oven at 40°C [13].

Fabrication of hydrophobic surface by phase separation technique explored by Wu et al. is adopted in our present research work [14]. PVDF base composite material used for fabrication of hydrophobic surface was prepared by mixing of 1 g PVDF and required amount of titania powder with varied concentration from 1 wt% to 5 wt% in 20 mL DMF followed by stirring process for 1 hr at 50°C. Then the mixture was ultrasonicated (Sonicator: Model-EI-6LH-SP, Sl. No-1209-122) at 20 kHz and 20 W for 30 min. The solution was poured in 50 mL deionised water under stirring process. Using vacuum filtration, precipitates were collected and further washed with 50 mL deionised water. The composites were dried 70°C for 8 hrs. Scanning electron microscopy (SEM 200, FEI) was used to evaluate the surface texture of PVDF/titanium dioxide composite hybrid. The water contact angles were measured with 4 μL water using a contact angle system (DSA100) under ambient conditions. The average value of five measurements at the different positions on the sample was adopted as the apparent contact angle.

3. Results and Discussion

In the present experimental procedure, water was used as nonsolvent, which induced phase separation and precipitation of polymers from the solution. Titania powder is preferred to precipitate with PVDF from the solution and led to phase separation. Figure 1 shows the value of water contact angle (WCA) obtained at various concentration of titanium dioxide powders. It is seen that PVDF containing 1 wt% TiO_2 exhibits water contact angle of 124°. With the increase in titania content from 1 wt% to 2 wt%, WCA is marginally increased from 124° to 129°. However, it is observed that with PVDF/titanium dioxide composite containing 3 wt% to 5 wt%, water contact angle was marginally decreased. With

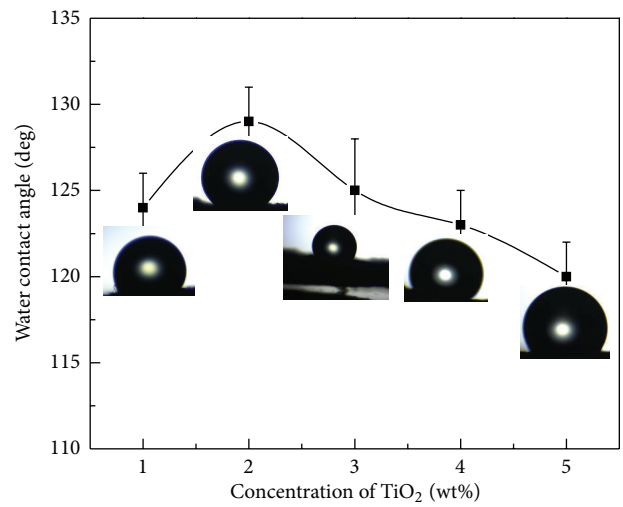


Figure 1: The variation of water contact angles of the PVDF composites with a different concentration of titanium dioxide.

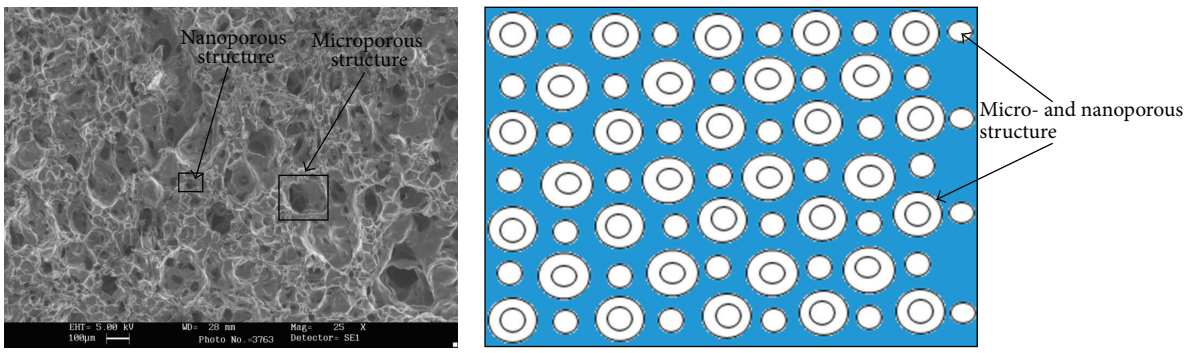
5 wt% TiO_2, composite shows water contact angle 120°. This result revealed that titanium dioxide concentration of more than 2 wt% has strong effect on wettability property above 2 wt%. With high concentration of titanium dioxide in the composite, all porous surfaces are covered.

Generally hydrophobic property of a film is controlled by chemical composition and surface roughness and is reflected directly from contact angle of droplet. According to the Wenzel model [15], water contact angle of a composite surface can be described as

$$\cos\theta_w = R\cos(\theta) = R\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}, \quad (1)$$

where θ_w and θ denote the Wenzel contact angle and Young's contact angle, respectively. Similarly γ_{sv}, γ_{sl}, γ_{lv} are the interfacial energy between solid vapor, solid liquid, and liquid vapor, respectively. R is termed as the roughness of the porous composite surface. From (1), it is clearly observed that contact angle increases with increasing value of R, if the contact angle on smooth surface is more than 90°. So it is indicating that more air trapped under the water droplet enhances the surface hydrophobicity [16]. So this trapped air acts as surface roughness and favours the enhancement of surface hydrophobicity, when the chemical composition of the surface is kept constant.

3.1. Surface Morphology of Composite Hybrid of PVDF/Titanium Dioxide. Figure 2(a) shows the surface morphology of dried composite mixture of PVDF/2 wt% titanium dioxide which exhibits mixture of nano- and microporous structure. The diameters of these nanoporous and microporous structures are 30–50 μm and 60–120 μm respectively. With incorporating 2 wt% titanium dioxide powders in the mixture, the hydrophobicity of composite surface was found to be maximum. But with addition of more TiO_2 powders, nanoporous structure becomes compact and percentage of air trapping reduces which leads to minimizing the



(a) (b)

Figure 2: (a) SEM images of the as-prepared polymer composite containing 2 wt% TiO_2. (b) Schematic presentation of PVDF/TiO_2 polymer composite.

hydrophobicity of the composite surface. Thus, increasing the concentration of titanium dioxide in composite beyond 2 wt%, reflects reduction in hydrophobicity. It is due to the deposition of titania particles as layer by layer on the nanoporous surface. Thus the water contact angle decreases from 1290 to 1200 with addition of titania powder which reveals reduction in hydrophobicity [17]. To understand the wettability property of composite surface, schematic diagram is shown in Figure 2(b). From schematic diagram, it is clear that more air is trapped in between the microporous and nanoporous structure, which enhances the surface roughness and improves the water contact angle. However, Amir and coauthors have made TiO_2/PVDF hollow fiber membrane, which showed water contact angle of 98°. They have observed that with the incorporation of TiO_2 powders in PVDF membrane, surface structure, porosity, and pore size do not change. But we have seen that with addition of more concentration of TiO_2 in PVDF composite, surface structure changed and hence decreased the hydrophobicity of the material but marginally decreased as compared to the reported literature [18].

4. Conclusions

In this work, we have discussed a facile approach for preparing hydrophobic surface using titanium dioxide as additive materials with nano- and microporous roughness and low surface tension in one step by the phase separation method. The rough surface was derived from nano/microporous structure and hence increases the hydrophobicity with water contact angle of 129°. 2 wt% titanium dioxide shows enhanced hydrophobicity (WCA, 129°). Further increase in titanium dioxide concentration leads to decrease in hydrophobicity due to increased compactness and air trapping reduction in the composite matrix. This method might provide the easiest route to prepare the large area of superhydrophobic coating for various automotive industry applications using additive titanium dioxide powder.

Acknowledgments

The authors appreciate the support of Dr. Prahlada VC, DIAT, for his continuous encouragement. The authors would also like to thank the "DIAT—NANO project EPIPR/ER/1003883/M/01/908/2012/D(R&D)/1416".

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