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Preparation of super water-repellent membrane by radiation-induced copolymerization ☆

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Abstract

Super water-repellent surfaces are generally introduced by controlling the surface chemistry and surface roughness, which are applied by means of complex time-consuming processes. We describe a simple method for forming super water-repellent surfaces using ^{60}Coγ irradiation induced hexafluoropropylene/ethyl methacrylate (HFP/EMA) vapor phase copolymerization under atmospheric pressure conditions. The resulting coral-reef-like microtexture surface has a water contact angle of 153°. The method described here could easily be extended to preparing superhydrophobic surface from a wide variety of materials.

PACS: 87.50.Gi, ionizing radiations; 68.08.Bc, wetting; 68.08De, structure/measurements and simulations
Keywords: Surface structure; Morphology; Roughness; Topography; Wetting; Radiation copolymerization; Hexafluoropropylene

1. Introduction

There have been continual demands for water-repellent surfaces, especially for extra water-repellent surfaces, which show water static contact angles (CA) greater than 150°, in a wide variety of fields, such as automobile glass, hulls of ships and pipelining, antennae, etc. [1]. The wetting behavior of solid surfaces, which are strongly dependent on both the chemical composition and the morphology [2] of the topmost layer, has been studied from both fundamental and practical perspectives. Up to now, many significant techniques have been developed to produce extra water-repellent surfaces, including the sol–gel method [3], microwave plasma enhanced chemical vapor deposition [4], plasma polymerization and modification [5], physical vapor deposition [6], chemical vapor deposition [7], phase separation [8], mixing powers of silica or PTFE [9], dispersion plating [10], molding [11], template-based extrusion method [12], laser etching [13], spray-and-dry method [14], electrochemical deposition [15] and hot filament chemical vapor deposition process [16]. All these methods have a common feature that super water-repellent surfaces are constructed by combining suitable roughness with low surface energy materials. The control of surface roughness is therefore essential in preparing super water-repellent surfaces. The second vital step is to modify the surface chemical property by low surface energy to enhance extra water-repellency. These methods generally require special apparatus operated under complicated conditions. Hence such techniques are not easily scalable.

Fluorocarbon materials show extremely low surface energies, and are confirmed to be the best material for producing surface modifiers for polymers [17,18], glass, textile, paper, and metal. Of all the materials on a flat surface, the lowest surface energy value was acquired from a surface with regularly aligned closest-hexagonal-packed CF_3 groups [19] and was calculated to be about 6.7 mJ/m^2. Hexafluoropropylene (HFP), packed CF_3 groups, and unsaturated fluorocarbon with F/C ratios of 2, should be suited for modifying materials to form low energy surfaces.

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However, homopolymerization of HFP only takes place under ultra-high pressure and high temperature [20] or plasma polymerization [21]. HFP can only copolymerize with vinyl monomers by different methods [22,23]. It is difficult to find a direct synthesis method for modifying the surface property with HFP under its vapor phase, despite its practical advantages.

In this paper, we report for the first time the superhydrophobic surface (CA=153°) on the PEMA membrane was gained through HFP/EMA vapor phase copolymerization by ^{60}Coγ irradiation under atmospheric pressure conditions. Compared to the super water-repellent systems mentioned above, our preparation method is much simpler and easily scalable. SEM, XPS and ATR-IR indicated that the upmost layer exhibited both microstructured surfaces and enriched fluorine. ^{60}Coγ irradiation induced HFP/EMA vapor phase copolymerization deposition exhibited practical advantages, in that it is possible to prepare large area superhydrophobic surfaces on many membranes, especially for complex surfaces.

2. Experimental

2.1. Materials

Ethyl methacrylate (EMA), from Shanghai Chemical Auxiliary Ltd., China, was freshly distilled under vacuum and stored in the refrigerator below 5 °C.

Hexafluoropropylene (HFP), from Jiangsu MeiLan Group, China, was stored in a standard gas cylinder.

2.2. Gamma radiation source

Gamma radiation induced polymerization was carried out in a reaction flask (Fig. 1). Irradiation was performed in a panoramic 100,000 Ci ^{60}Co irradiator, having an activity of 80,000 Ci during the period of the experiments. The dose rate, measured by a Fricke dosimeter, has been from 7.8 Gy/min to 26.7 Gy/min.

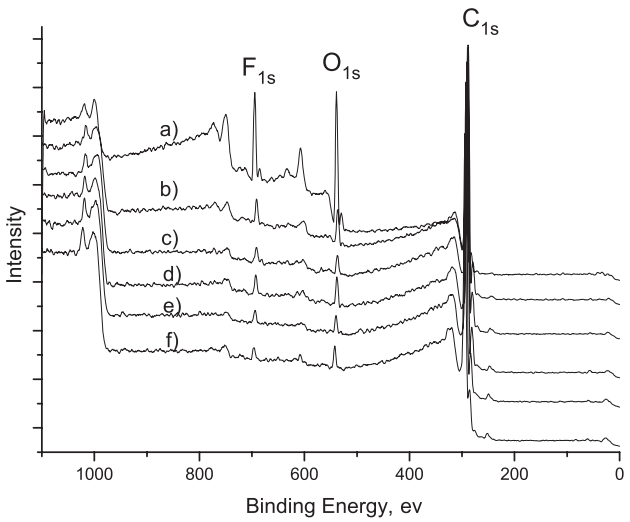

Fig. 2. XPS spectra of the deposited surface (a) without Argon sputtering; (b) after argon sputtering (30 s); (c) after argon sputtering (60 s); (d) after argon sputtering (90 s); (e) after argon sputtering (120 s); and (f) after argon sputtering (180 s).

2.3. Characterization

X-ray Photoelectron Spectroscopy (XPS) analyses were performed with an ESCALAB MK-II (VG instruments), using an aluminum Kα monochromatized X-ray source. The binding energy shift from the surface charging of the polymers was overcome by the use of an electron flood gun at 4 eV, vacuum level at 10^{-9} mbar, voltage at 12.5 kV, electric current at 20 mA.

The composition of the surface was determined using a Nexus 870 FT/IR equipped with an ATR attachment provided with an OMN1-Transmission with the incident angle $\theta=45°$ and a Ge element with $\theta=45°$.

Contact angles (CA) of liquid droplets placed on the surfaces were measured by an optical contact angle meter (CAM200 of KSV Instruments Ltd., Finland). The volume of the droplet was about 5 μl. Images of a drop are acquired, and the CA is determined by image analysis software, which is base on a numerical integration of the Laplace equation of

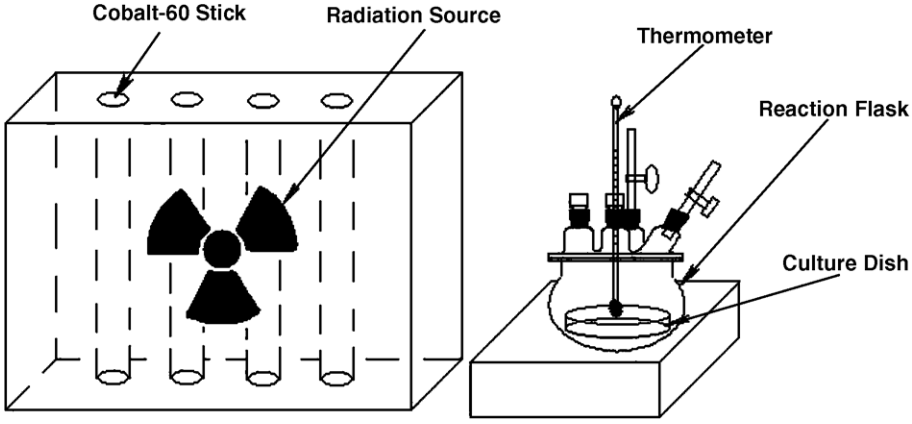

Fig. 1. A schematic of gamma radiation induced polymerization system.