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Two types of oil modified tips as force sensors to detect adhesion forces between oil and membrane surfaces in fluid

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ABSTRACT

The surface resistance to oil is very important for filtration efficiency, film cleaning and life span of ultrafiltration membranes. The atomic force microscope (AFM) has provided unprecedented opportunities to study interface interactions. In this paper, the probe with an oil droplet modified was used as a force sensor for evaluating the oil resistance of membrane surfaces. The adhesion forces between two types of modified tips and a serial of membrane surfaces in fluid was detected via force curves. On the one hand, the AFM probe with an oil droplet immobilized directly was used to study the adhesion forces between a series of PVF/F127 membranes and a hexadecane droplet. On the other hand, a tip attached polystyrene (PS) microsphere covered with a layer of oil was employed. It was found that the oil antifouling performance of membranes was improved effectively through blending F127 with PVF. As the F127 additive varied from 0% to 60%, adhesion force detected by the AFM probe with an hexadecane droplet immobilized showed a decreasing tendency from 2.84 nN to 0.73 nN. Meanwhile, the average interaction force detected by the second modified tip decreased from 3.39 nN to 0.54 nN. The measured force behavior was in agreement with experimental observations of contact angle measurement, which indicated that the blend membranes had better antifouling.

1. Introduction

With the development of the petrochemical industry, emissions of oily wastewater are increasing and environmental problems have become a great challenge. Membrane technology is regarded as the most efficient approach for advanced wastewater treatment and reuse, owing to its advantages of low energy consumption, high separation efficiency, low environmental pollution, flexible and simple process and strong versatility. However, oil droplets may directly come into contact with membrane surfaces in reality. The inherent oil fouling often leads to a cascade of events, such as adhesion, accumulation, spreading, coalescence and migration of suspended oil foulants, which is much more complicated than the fouling caused by soluble organic macromolecules and insoluble inorganic matter [1]. As a result, the gradual coalescence and migration of oil droplets form a continuous oil film and cause a sharp decline of permeation flux temporarily or permanently, leading to a reduced life span of the membranes.

Superhydrophilic-superoleophobic films utilize "water-removing" method [2] that effectively prevents the adhesion of oil droplets and could be applied to the mixture with small percentages of oil, and it is usually selected because of its low energy consumption. Researches show that the hydrophilicchemical materials and micro/nano composite structure are the key factors to design antifouling membrane surfaces [3,4]. Surface modification, physical blending and chemical grafting are mostly adapted to improve the membrane hydrophilicity and fouling resistance. Among these methods, blending has been extensively applied due to its versatile controlling conditions.

Filtration test [5,6] and adsorption test [7] evaluate the antifouling performance of membranes on the macroscopic level. Filtration test usually takes ∼3 h for one membrane, which is time-consuming. Adsorption test has the same problem. Contact angle measurement [8] evaluates the antifouling property of films by measuring the geometrical shape of oil droplets on films, which can only evaluate the hydrophilic property of materials. It belongs to point measurement method. And the result has certain contin-

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gency and randomness. Pore analysis [9,10] and surface roughness evaluation [11] are methods to explore the relationship between structural parameters and antifouling property of membrane surfaces. They can only be used as a reference and comparison of other methods. The methods discussed above are all on the macroscopic level. However, a quantitative and accurate measurement of the force between the oil and the sample membranes in microscopic aspect can be made. The atomic force microscope (AFM) can be used to estimate the interaction between membrane surfaces and pollutants modified on the tip of the special AFM probes, which is one of the most direct methods to assess the antifouling property of membranes. Hence, AFM probes are sensitive force sensors to convert interaction force between them to the deflection of the cantilevers. Finally, the interaction force is calculated by several parameters. It is well-known that a bovine serum albumin (BSA) protein immobilized tip must be obtained by a series of complicated steps, such as vacuum oxygen plasma method, chemically modification and so on. It is used to evaluate the bio-antifouling properties of the membrane. The new methods discussed in this paper aim at evaluate the oil-antifouling performance of the membrane and they are more simplified and efficient. However, the approach to modify an oil droplet on the tip of the cantilever is different from the traditional method of protein modification. The protein cluster can be fixed on the tip by the strong interaction of chemical bond [11,12], which is generally considered to be a rigid connection with the same structure. The oil droplets would not be stable in air, so the oil droplet modification must be carried out in the liquid phase. After the modification, it must ensure that the fixed position of the oil drop is always the same during the whole experiment. In addition, oil droplets are flexible structures. It is worth discussing whether the loss of the oil droplet during the testing process will have an influence on the results.

The size of AFM cantilevers and the micron dimension of oil droplets are well matched. The cantilever with a micron oil droplet modified can be used as a high sensitive sensor for the measurement of adhesion between oil pollutants and films, which can be expected to be an effective method of membrane antifouling evaluation in microscopic aspect. In this paper, two methods are adopted to transfer a target oil droplet on the tip of a bare cantilever. A series of polyvinyl formal (PVF) membranes with different percent of additive F127 were prepared via non-solvent induction phase separation process. F127 was usually used as a surface segregation additive to construct a hydrophilic brush layer on the membrane surface and to further improve the antifouling performance of PVF membranes. The adhesion forces between the blend membranes and the oil droplets (hexadecane) on the AFM tips were measured in order to compare the antifouling property of the membranes. But the shortcoming of these methods lies in the wide range of the spring constant of the commercial AFM probes. So it is necessary to calibrate the AFM cantilevers and only the data from just the same cantilever is comparable. Moreover, comparison experiment of contact angle measurement has also been done for analysis and comparison.

2. Material and methods

2.1. Materials

Polyvinyl formal (PVF, MW = 35 kDa, acetalization degree = 80%) purchased from Tokyo Chemical Industry Corp. (Japan) was dried at 60 °C for 12 h before use. Triblock copolymer Pluronic F127 (EO_{100}-PO_{65}-EO_{100}) with Polyethylene oxide (PEO) content of 70 wt% was purchased from Sigma Chemical Company (USA). Preparation of PVF/Pluronic F127 membranes was described in the previous study[13]. NP-O10 probes made of silicon nitride were purchased from Bruker Corp. (Germany). HA-C/tipless probes made of polysilicon were purchased from NT-MDT Corp. (Russia). Hexadecane were obtained at >99% (Sigma Aldrich). Polystyrene (PS) microspheres and special glue were provided by School of Material, Tianjin University. All silicon wafers were carefully cleaned with ethanol through ultrasonic cleaning machine (KQ3200E, China). Other chemicals were purchased from Kewei Chemicals Corp. (China).

2.2. Interaction forces between an oil droplet-immobilized tip and membrane surfaces

2.2.1. Preparation of oil droplets

Two micropipettors (0.5–10 μL and 20–200 μL) were used to prepare hexadecane droplets in the following manner. Firstly, a silicon wafer was cleaned by ultrasonic cleaning machine. Then the hexadecane was sucked into a 0.5–10 μL micropipettor and pure water was sucked into a 20–200 μL micropipettor. Finally, it is better to direct micropipettor containing hexadecane approximately 4 cm over the top of the slide and to add pure water onto the silicon wafer quickly after squeezing it, in order to create a fine spray of hexadecane droplets which was dispersed over a clean silicon wafer. It was found that this method resulted in a fairly uniform coverage of the slide with discrete 10–40 μm diameter oil droplets.

2.2.2. Attachment of oil droplets onto the AFM cantilever

The AFM head holding NP-O10 tipless cantilever (Si_3N_4) was positioned directly above a droplet on the surface of the silicon wafer. Then it was lowered down in order to sandwich the water between the cantilever holder for fluid operation and the silicon wafer. And it was advised to adjust the value of setpoint during this period. Once engulfment of the hexadecane droplet had been achieved, the AFM head and cantilever were retracted away from the surface of the slide, where upon the oil droplet was found to detach itself from the slide surface. This method allowed the

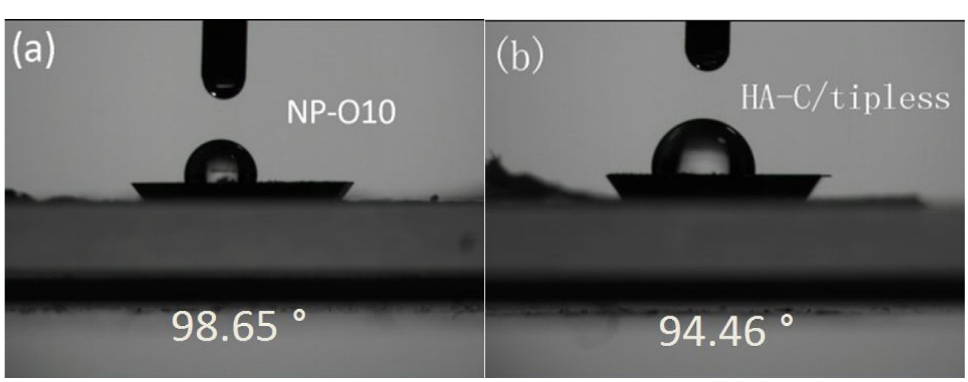

Fig. 1. Images of water droplets on the probe surface in air.