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Short Communication

Synthesis and evaluation of polystyrene–polybutadiene–polystyrene–dodecafluoroheptyl methacrylate/polystyrene–polybutadiene–polystyrene hybrid antifouling coating

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ABSTRACT

Copolymers SBS–DFHMA and mesoporous silica SBA-15 were respectively synthesized and SBS–DFHMA were mixed with SBA-15 to prepared hybrid antifouling coatings by a spin-coater. By measuring the surface water contact angle and the attachment of *Pseudomonas fluorescens*, Chlorella and Diatoms, the antifouling properties of coatings were evaluated. The results shown that the surface of hybrid coatings, the water contact angle arrived 120°, were more hydrophobic than the SBS–DFHMA coatings. In terms of resistance of adhesion, low surface energy coatings of SBS–DFHMA could effectively weaken the adhesion behavior of *P. fluorescens* and Diatoms, but the role to Chlorella was not obvious. When 0.01 g/ml SBA-15 was added, the adhesion of three marine microorganisms all had a very significant decrease to the hybrid coatings. These indicated that the fluorinated low surface energy antifouling coatings had limitation on resisting Chlorella attaching, and the addition of SBA-15 not only enhanced the ability of resistance to adhesion but also widen the applicability to more fouling and narrowed its limitations. This surprising effect was due to micro–nano convex structure of the coatings surface caused by hybrid.

1. Introduction

With the growing awareness of environmental protection, the original anti-fouling paints, organic tin [1] was used as anti-fouling agent, which were harmful to environment will be gradually replaced by environment-friendly products. The current antifouling paints of cuprous oxide still impact on the environment [2]. So, the research of new product to meet the needs of industry and environment are required imminently.

It has been demonstrated that the adhesion strength of hard fouling organisms is proportional to $(\gamma E)^{(1/2)}$, where γ is the surface energy and E is the modulus of the surface [3,4]. Low surface energy antifouling coatings are one of the directions to seek a breakthrough to researchers in the current. This type of coatings usually refers to organic fluorine or silicone resin that introduce the fluorine-containing or silicon-containing groups to organic resin through a series of reactions [5,6]. Compared to silicon-containing coatings, fluorine-containing coatings cause lower surface energy, because fluorine atom is much smaller and more polar, easier to capture electrons to be a stable structure and more hardly to form the van der Waals force with any other groups, which may endue the fluorine-containing resin with superior performance as an antifouling coating material [7]. Unfortunately, these materials are typically hard and brittle with high modulus and do not provide sufficient releasing of marine biofouling. Thermoplastic elastomers such as polystyrene–polybutadiene–polystyrene (SBS) block copolymers offer desirable mechanical properties (relatively low modulus), low cost, wide application, easy modification and good plastic viscosity and workability, but undesirable surface characteristics. Thus, in this experiment, a strategy to incorporate both of these previously described favorable properties, by combining polystyrene–polybutadiene–polystyrene (SBS) and dodecafluoroheptyl methacrylate (DFHMA) to obtain a fluorine-containing copolymer (SBS–DFHMA) which will be used to prepare the low surface energy antifouling coatings, is expected to offer excellent fouling control.

Since the synthesis of mesoporous silica SBA-15 was first reported in 1998, it had attracted wide attentions [8]. Many researchers treated it as a carrier to load metal or oxide to use in the field of catalyst, and also for loading drugs [9,10]. Relevant experiments in our lab had suggested that SBA-15 was used to load

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the enzyme that can effectively protect the activity of the enzyme, and enhance its reuse. In this experiment, the fluorinated low surface energy antifouling coatings mixed with SBA-15 which can be used to load nano antifouling agents or enzymes that may have the prospects for improving antifouling properties of the coating. During the process, SBA-15 surprising enhanced the hydrophobicity of the coatings, which may affect the antifouling property. Accordingly, on the base of researching the antifouling property of fluorinated polymer, experiments focused on exploring the development of the antifouling performance with SBA-15 of the hybrid coating.

2. Experimental section

2.1. Materials

The polystyrene–polybutadiene–polystyrene polymer (SBS) and dodecafluoroheptyl methacrylate (DFHMA) were supplied by Shanghai Sunvea Chemical Material Co., Ltd. The azodiisobutyronitrile (AIBN) was crystallized from an industrial product (Tianjin Guangfu Fine Chemical Research Institute). The poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123) was purchased from Sigma–Aldrich and used as received. The other chemical reagents were used as commercially received from Sinopharm Chemical Reagent Co, Ltd. *Pseudomonas fluorescens*, Diatoms and Chlorella were supplied by Guangdong Microbiology Culture Center.

2.2. Preparation of the copolymer (SBS–DFHMA)

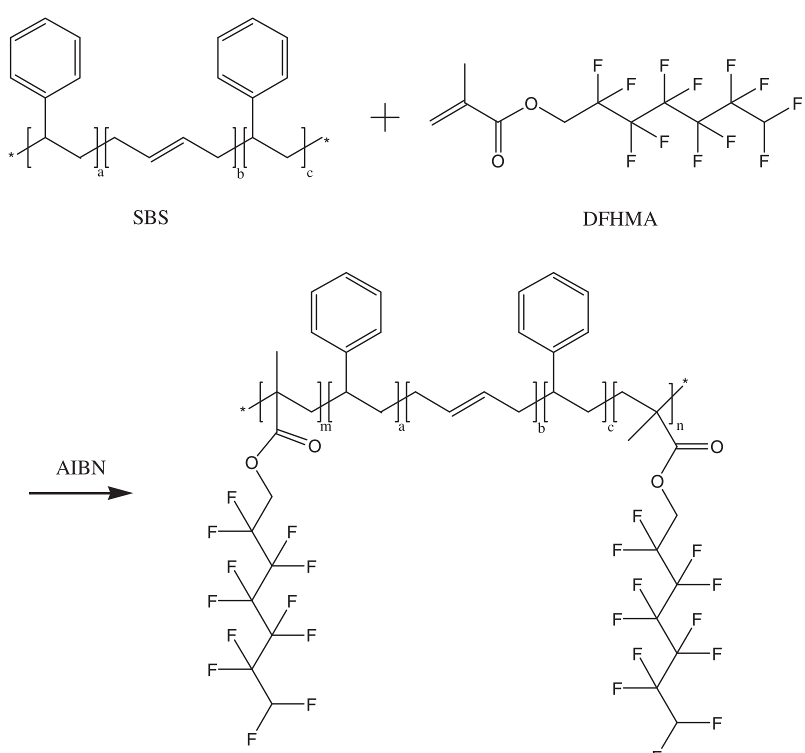
10 g of SBS and 100 mL of tetrahydrofuran (THF) were taken in a 500 mL round bottom flask and stirred for 0.5 h at room temperature. Then 20 g of DFHMA and 0.1 g of AIBN were added to the flask and stirred for 5 h at 65 °C. The reaction mixture was left overnight and followed by adding to 300 mL of ethanol on stirring. The product precipitated from the solution was filtrated and washed with 2×30 mL of ethanol. After dried in a vacuum oven at 50 °C for 1 h, 14.5 g of the white resin-like material (SBS–DFHMA) was obtained. The ^1H NMR spectra were recorded on a Mercury plus 400 instrument (Varian) for solutions in $CDCl_3$ using $(CH_3)_4Si$ as an internal standard. ^1H NMR for SBS–DFHMA (400 MHz, $CDCl_3$, δ):7.12, 6.61 (Ar—H); 5.44, 5.00 (—CH=CH—); 3.77 (—O—CH_2—CF_2—); 2.06 (—C—CH_2—C—); 1.45 (—CH_2—C=C—); 0.01 (—C—CH_3). The infrared spectra (IR) were recorded on a Tensor 27 FT-IR Spectrometer (Bruker). IR (dry film) υ max (cm^{-1}): 3083, 3058, 3026 (C—H stretching, aromatic); 3006 (=C—H stretching); 1244 (O=C—O stretching); 1215 (C—F stretching); 751, 697 (C—H bending, aromatic). The number–average, weight–average and viscosity–average molecular weight were measured as 116,500, 118,800 and 121,100 respectively by a gel permeation chromatography system (HLC-8320GPC EcoSEC, Tosoh) using tetrahydrofuran (THF) as mobile phase and polystyrenes as the standards.

2.3. Preparation of the mesoporous silica (SBA-15)

The mesoporous silica SBA-15 was prepared according to the literature [11]. The XRD analysis of the mesoporous silica (SBA-15) was conducted on a D8 Advance X-ray diffractometer (Bruker AXS). The morphology analysis was analyzed by a S-3000N scanning electron microscope (Hitachi). The nano structure was analyzed by a Sirion 200 transmission electron microscopy (FEI). The N_2 adsorption–desorption isotherms and pore sizes of the mesoporous materials were measured on an ASAP 2010 surface area and porosimetry analyzer (Micromeritics).

2.4. Preparation and characterization of the hybrid coating (SBS–DFHMA/SBA-15)

1.0 g of the block copolymer (SBS–DFHMA) was dissolved in 10 mL of THF, and different quality (0.1 g, 0.2 g, 0.3 g) of SBA-15 was added respectively. The mixture was stirred at room temperature for 2 h and then spined on a clean glass slide. After evaporation of the solvent, the hybrid coatings were then obtained for



Scheme 1. Structure of fluorinated copolymer (SBS–DFHMA).