Progress in Organic Coatings 124 (2018) 158–164

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Fluorine-free coating with low surface energy and anti-biofouling properties

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ARTICLE INFO

Keywords:
Silicone
Tris-Trimethylsilypropyl methacrylate
Low bio-adhesive coating

ABSTRACT

Infection caused by bacterial colonization on medical devices is a significant problem in clinics. Low surface energy of bio-adhesives can resist microbial colonization or minimize adhesion between microbial and surface. Such surfaces are becoming more widely investigated for possible use in various applications, such as biomedical and biological applications and cell-based assays. In this paper, a series of tris(trimethylsiloxy)silyl (M_3T) containing methacrylate copolymer with low surface energy were designed and synthesized, and the surface and mechanical properties of copolymer coatings were characterized. The results show that the amount of curing group trimethoxysilane propyl methacrylate (TMOSPMA) and rigid building block propyl methacrylate (PMA) had significant effects on the surface and mechanical properties of copolymer coatings. More curing group and more rigid component resulted in better mechanical property. The random terpolymer (M_3T-co-PMA-co-TMOSPMA) with a molar ratio of 2/8/3 formed hydrophobic coating with good mechanical properties with respect to B hardness. The cell and bacterial growth test showed that the coating had low cell adhesion property and good anti-bacterial performance.

1. Introduction

Biofouling is the accumulation of bacterial on surfaces, which commonly occurres in the biological world. Biofouling of underwater structures and ships' hulls results in increased operational and maintenance costs. Biofouling of medical devices causes the function of the device to be impaired and infections. Low bio-adhesive surface can resist colonization by microbial or minimize adhesion between microbial and the surface of a material. Such surfaces are becoming more widely investigated for possible use in various settings [1,2] including clinics, industry, and even the home. The most common and most important use of low bio-adhesive coatings has been in marine [3–11], biomedical and biological applications [12–18] for a long time. For example, low bio-adhesive coatings are used in devices for cell based and protein based assays, in medical devices [19–22] such as injectable cell delivery vehicles, in CT or MR machines, in surgical devices, in devices for immunoisolation-based therapies and in other in vitro or in vivo usages.

Low bio-adhesive features can be achieved by different surface modifications and coating techniques [23,24], including direct impregnation with antibiotics [25,26], coating with antimicrobial metals such as copper and silver [27–31], super-hydrophobic coating, hydrophilic polymer coating [32,33] combined with plasma ablation [34–38]. However, most of the above surface modifications and coating processes are complex and expensive, on the other hand the hydrophilic surface provides a bridge for liquid transfer between spots, resulting in inter-contamination. Therefore, it would be highly desirable to develop a simple and cost effective biocompatible low bio-adhesive coating for use in such applications. Polymeric low surface energy polymer coating [39–42] has shown high commercial potential due to the simple process and low cost. Fluorinated materials are the most popular low surface energy coating materials, however US Environmental Protection Agency (EPA) issued tight regulations on fluoropolymers, which could release highly toxic materials such as perfluoroalkyl carboxylates, or perfluoroalkyl sulfonates into environment. Accordingly, the identification of non-fluorinated coating with low surface energy and little environmental and health concerns draws more and more research interests.

Beside fluorinated materials, silicone and olefin are materials with very low critical surface tension. In the previous paper [43], tris(trimethylsiloxy)silyl (M_3T) containing methacrylate copolymers (Fig. 1) were designed and synthesized, low surface energy and good anti-stain performance were demonstrated. Surface energy and mechanical properties are two important features to low bio-adhesive coating application. Therefore, the critical issue to be resolved in this paper is to optimize M_3T-containing methacrylate copolymers structure to achieve

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https://doi.org/10.1016/j.porgcoat.2018.07.036
Received 11 February 2018; Received in revised form 13 July 2018; Accepted 28 July 2018

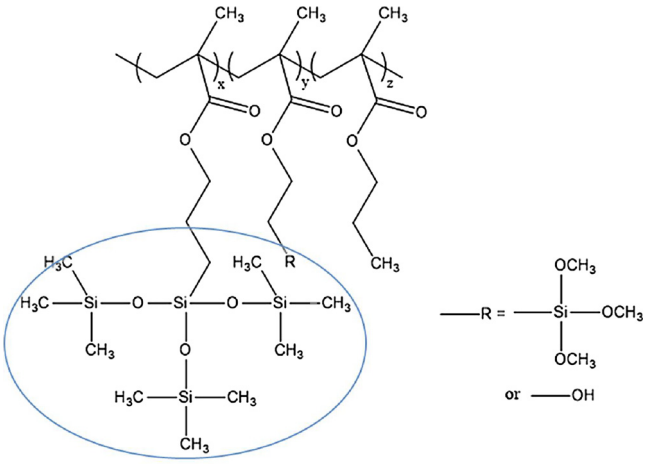

Fig. 1. Chemical structure of M_3T containing polymer.

both low surface energy and good mechanical properties. Curable function and organic polymer segments are incorporated to enhance mechanical properties and silicone functionality is to provide desired surface properties. The umbrella-like alignment of M_3T groups on the coating surface is expected to offer low surface energy to prevent the substrate from the attachment of cell and bacterial. Trimethoxysilylpropyl methacrylate (TMOSPMA) and 2-hydroxyethyl methacrylate (HEMA) monomer units crosslink the coating into a dense network and give good mechanical properties. After the optimized coating formulation is identified, the cell growth and anti-bacterial test are performed. The silicone based coating shows low cell adhesion property and good anti-bacterial performance.

2. Experimental

2.1. Synthesis of tris-trimethylsilylpropyl containing methacrylate copolymer and preparation of coating on different substrates

The detail synthetic approach for tris(trimethylsiloxy)silyl (M_3T) containing methacrylate copolymers was described in the previous paper [43]. Then the prepared copolymers were applied to different substrates for performance evaluation. The substrates including carbon steel panels, stainless steel, polystyrene Petri dishes, glass slides were washed with isopropanol and dried at room temperature. For the carbon steel panels, the anti-corrosive undercoat Safeguard Universal ES (from Jotun) was firstly applied to the carbon steel panel. In a detailed process, 5 parts Comp. A (base) was mixed with 1 part Comp. B (curing agent) using a high speed mixer. This composition was then applied to the carbon steel panel using a 300 μm draw-down bar, followed by curing at room temperature overnight. For other substrates, the anti-corrosive undercoat is not needed. All the prepared substrates were stored in a sealed container until the next step. The synthesized copolymers were concentrated to the required concentration (about 30% by weight) by rotary-evaporation, mixed with catalyst or/and curing agent (about 1 wt% of the pure copolymer), then applied to the substrates using a 300 μm draw-down bar and finally cured at room temperature for 5 days or at 80 °C for 4 h.

2.2. Coating performance evaluation and characterization

2.2.1. Polymer structure and coating surface/mechanical properties characterization

The structures of the copolymers were examined using a Bruker Avance 400 MHz NMR spectrometer, and the Component Analysis software invented by the GRC NMR team was used to analyze the components of the copolymers. The water contact angles of the coatings were measured by an OCA 20 instrument (DataPhysics). The coating hardness was tested by the pencil hardness tester (PPH-1, 1000 g, Shanghai Xiandai Environment Engineering Technique Co., Ltd) following the standard procedure.

2.2.2. Anti-bacterial property characterization

Bacterial cells, *Pseudomonas fluorescens* (from ATCC) were grown on stainless steel surface with coating of copolymer M_3T-co-PMA-co-TMOSPMA and on uncoated stainless steel surface at 30°C for 24 h. The bacterial cells grown on uncoated or on coated surface were removed from the stainless steel coupons and suspended in 35 ml of 0.85% phosphate saline buffer. The bacterial suspension was diluted by different times and seeded onto a 3M™ Petrifilm™ test plate (Petrifilm plate was used to calculate the amount of aerobic bacteria, which was a ready-made medium system for aerobic bacteria that contained standard method nutrients, cold water soluble gelling agents and an indicator for promoting colony counting), followed by culturing the bacteria at 30°C for 48 h. The bacterial colonies attached to the test plates were counted by a 3M™ Petrifilm™ plate reader. The total number of bacteria on different surfaces calculated by colonies of each bacterial sample at different dilution times.

2.2.3. Mammalian Cell adhesion property characterization

Mammalian cell adhesion was examined for uncoated and coated surfaces. Chinese Hamster Ovary (CHO-K1) cells and human breast cancer cells (MDA-MB-231) were purchased from ATCC. The culture media used for growing cells was Leibovitz's L-15 and was purchased from ATCC. Cells were seeded and cultured onto coated and uncoated glass slides and on coated and uncoated polystyrene Petri dishes. Uncoated and coated glass slides were placed into mammalian cell culture plates (having diameter of 6 cm). Suspended CHO-K1 cells were added onto each plate, and the plates were incubated at 37°C, in the presence of 5% CO_2 for 48 h in a CO_2 incubator. The slides were observed under Phase Contrast Microscope and the microscopy images clearly distinguish the uncoated and coated slides with respect to cell growth.

The copolymer M_3T-co-PMA-co-TMOSPMA was applied as a coating on a selective area of a surface of a polystyrene Petri dish (having diameter of 35 mm). This selective surface coated Petri dish was used to test cell growth on both coated and uncoated area. Human breast cancer cells (MDA-MB-231) were seeded onto the surface of the polystyrene Petri dish and incubated at 37°C for 2 h. The cells were stained with CellTracker™ Green CMFDA (5-chloromethylfluorescein diacetate). After 2 h of growth, the dishes were rinsed briefly by phosphate buffered saline (PBS) followed by taking a micro-image at 4x magnification and a macro-image by using a fluorescence plate scanner at Excitation/Emission at 488 nm/535 nm. CellTracker™ reagents are fluorescent chloromethyl derivatives that freely diffuse through the membranes of live cells. Once inside the cell, these mildly thiol-reactive probes react with intracellular components. Therefore, the cells produced from the parent cells are both fluorescent and viable for at least 24 h after loading of this reagent. CellTracker™ Green CMFDA has a relatively low pKa, which ensures that it will exhibit bright, green fluorescence in the cytoplasm at all physiological pH levels. Fluorescence image can clearly show cell growth on coated and uncoated area.

3. Results and discussion

3.1. Coating properties of copolymer (tris-trimethylsilylpropyl methacrylate-co-2-hydroxyethyl methacrylate) (poly(M_3T-co-HEMA))

The copolymers (tris-trimethylsilypropyl methacrylate -co- 2-hydroxyethyl methacrylate) (poly(M_3T-co-HEMA)) with different