Environmentally friendly self-polishing anti-fouling coatings for marine applications

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Abstract

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Marine environment is highly prone to fouling for all water-immersed surfaces. This causes huge burden on marine vessels and structures. Environmental friendly coatings are highly desirable to replace existing toxic coatings. Extensive efforts have been devoted to the development of environmental friendly and effective anti-fouling marine coatings. We have developed zwitterionic self-polishing coatings, which combine self-polishing and non-fouling properties for long-term performance for applications including marine. Non-fouling behaviors are studied by enzyme-linked immunosorbent assay (ELISA) while self-polishing behaviors are followed by weight loss. By varying the composition of coatings, self-polishing rates and non-fouling behaviors can be controlled.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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INTRODUCTION

Bio-fouling

Marine bio-fouling is defined as accumulation of biological organisms such as microorganisms, seaweeds, fungi, tubeworms and barnacles on marine surfaces immersed in seawater. The fouling processes as shown in Figure 1 usually consist of three main steps [1]: accumulation of organics adsorbed on surfaces (or conditioning film formation), micro-fouling, and macro-fouling.

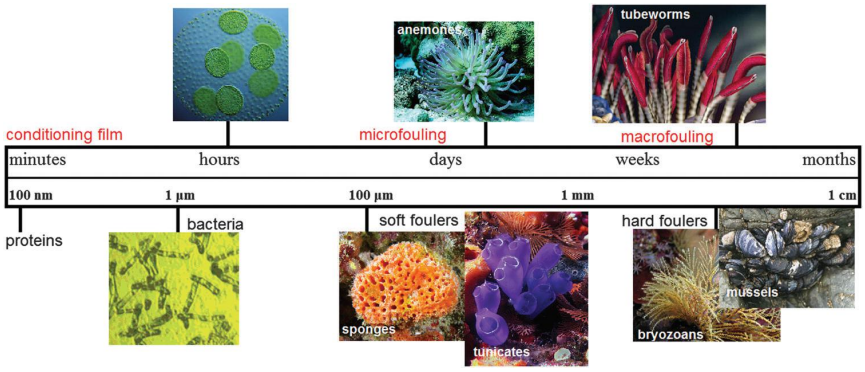

Fig.1 Different phases of marine bio-fouling [2]

Bio-fouling can result in severe adverse effects such as high resistance and thus high fuel consumption. The emission of harmful compounds is also increased accordingly. The Office of Naval Research (ONR) mentions in its website that “On its course, a ship can add barnacle weight at 150 Kgs per square meter in as little as six months. The Naval Surface Warfare Center, Carderock, estimates that vessel speed is reduced by up to 10 percent from bio-fouling, which can require up to a 40 percent increase in fuel consumption to counter the added drag”.

Conventional anti-fouling paints release toxic substances such as copper. Due to the increased application of copper in anti-fouling paints, copper concentrations have elevated in the areas of high boating activities, leading to environmental hazards.

Fig. 2 Examples of heavily fouled hulls[3]

Development of Marine Coatings

Bio-fouling is a well-known problem since men started their sea voyage. There is a rich history for people to develop coating technologies. Natural products, for example, waxes or asphalt, were the first materials to be used. Before the late 18th century, different materials were tried such as coatings containing arsenic with oils, leading sheadings and resins. The anti-fouling coatings were developed due to the development of iron ships. Among anti-fouling paints, tributyltin (TBT) self-polishing co-polymer coatings had been used extensively, which contain three main ingredients: anti-fouling agents, self-polishing resin and other additives. When the coatings are immersed in seawater, soluble elements in the top coating layer are dissolved. Seawater is then allowed to fill in and reacts with functional groups on surfaces, releasing tin metal ions under slightly alkaline conditions. The individual polymer chains in the top layer transform from hydrophobic to hydrophilic upon hydrolysis and finally dissolve in seawater and are washed away by water flow. This means that coatings are peeled away layer by layer in

seawater. Tin metal ions, which are released at the certain level of concentrations, are able to kill microorganics and prevent microorganism adhesive on coating surfaces. However, TBT-self polishing coating (SPC) system affects adversely the environment. For example, when TBT at a higher than tolerant concentration, it causes defective shell growth in the oyster.

The usage of biocide-release marine coatings is limited due to their disadvantages for the environment. 'Green' alternatives to biocide-based technologies are urgently sought by the marine coating industry. There are only two strategies to combat marine bio-fouling apart from toxic marine coatings: 1) fouling-release (FR) coatings (Fig.3b) and 2) non-fouling/anti-fouling coatings (Fig.3d). Fouling-release coatings are usually made of soft polydimethyl siloxane (PDMS)-based polymers. Although these coatings are used, they are usually fouled due to their inherent hydrophobicity under slow-moving ships. Biocide-free anti-fouling polymers such as zwitterionic or poly(ethylene glycol) (PEG) are non-fouling. Since their superhydrophilicity, they are highly soluble in water and have practical barriers to be used in the marine environment.

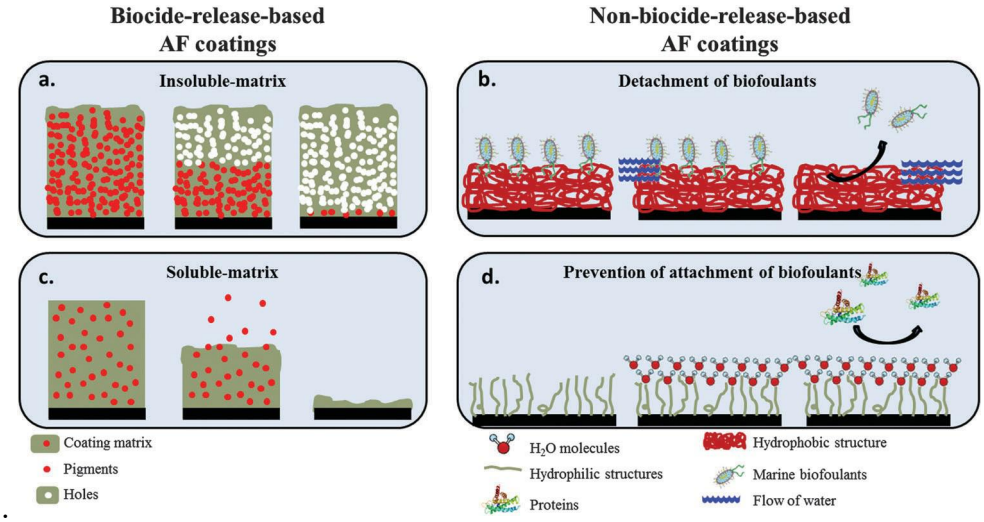

Fig. 3 Biocide-release (a and c) and non-biocide-release (b and d) based strategies [2].

Hydrogels are also used as environmentally friendly anti-fouling materials. Many groups focus on these soft materials such as acidic hydrogels of PAMPS (2-acrylamido-2-methyl-1-propanesulfonic acid) and PAA (polyacrykic acid) [4]. But, due to their weak mechanical properties, hydrogels are harder to be used in the marine environment where long-term performance and stability are the main requirements.

Mixed-charge Structure

Adhesion of organic adhesives is the first step of bio-fouling on a surface. There are four adhesion mechanisms for organic adhesives to stick to surfaces.The non-polar moieties are the first mechanism. Electrostatic interactions are the second mechanism to prevent the presence of polar, heteroatoms and ionic groups at the interfaces. Mechanical interlocking is the third mechanism, which can be avoided by having a smooth surface. The last mechanism is temporary microvoids and biofoulants inward diffusion. All of these mechanisms require different solutions.

In biological environments, proteins are generally the first step of bio-fouling. Hence, it is highly desirable to prevent protein attachment. If protein adhesion can be prevented, then all kinds of adhesive organisms can be reduced or eliminated. Zwitterionic or mixed-charge material is defined as the one, which contains roughly equal amount of positive and negative. Due to the charges, the hydration ability of this material is relatively strong. Upon hydration, a layer of water will stay on the surface and this layer can prevent non-specific protein adsorption. Hence, settlement of microorganisms can be avoided. To achieve long-term stability, the polymer has a hydrolysable group, which is hydrophobic in the beginning and becomes hydrophilic upon hydrolysis. The resulting coating is self-polishing and nonfouling. The behavior of the coatings

can further be adjusted as needed by additional crosslinkers or counter ions. These mixed-charged coatings are environmentally friendly as compared with conventional coatings containing metal ions or organic biocides.

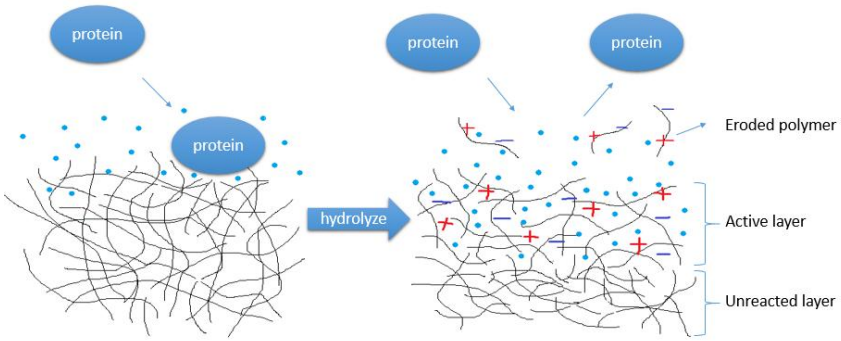

Fig. 4 Upon hydrolysis, the surface becomes hydrophilic and non-fouling due to the mixed-charge structure.

MATERIALS and Experimental Methods

Protein

Fibrinogen from human plasma (≥90%) was used for fouling test. This protein was purchased from Sigam-Aldrich.

Solvents

Chlorobenzene (Sigam-Aldrich) and methanol (Fisher Scientific) were used as solvents for polymer synthesis.

Polymer Synthesis

Monomers, counterion, and initiator were weighed to appropriate molar ratios. The total amount of polymer is kept at 10g. The ratios between positively and negatively charged monomers were adjusted for different formulations. The amount of initiator was 1% wt of monomers. The monomers were dissolved in a solvent with a weight ratio of solid content between 10-50%. In order to remove oxygen in the flask, the polymer solution was bubbled with nitrogen gas for 20 minutes. The flask was then moved to an oil bath preset at 70C and the reaction was continued for two days.

Panel preparation

For laboratory and external studies, fiber glass panels were used. The fiber glass panels were sand-blasted to generate artificial roughness. The panels were then rinsed with water and acetone to remove all small particles on the panel surfaces. The panels were then air-dried.

Coating

For each panel (~30-50 sq.in), 10-14g polymer solution was used. Prior to coating, an epoxy crosslinker was optionally used as an additive. The amount of crosslinker was changed from 0% to 50% with respective to the mole of amine. The polymer solution was then drop-casted on the fiber panels and allowed to dry in room temperature. The panels were kept for drying for 3 days.

Weight-lost Study

In order to test self-polishing properties, a gravitational method was used to measure the weight loss of coatings by soaking in artificial seawater (ASW).

1. For this study, 2x2 inch square fiber glass sheets were used. Sand-blasting, followed by rinsing with a solvent, was carried out.
2. The panels were air-dried for 2 days.
3. Empty weight of the panels was measured.
4. Copolymer formulations were applied onto the sheets. Let sheets dry for 3 days.
5. Weight sheets were weighted initially and the polymer solution weight was calculated.
6. All the samples were soaked in ASW. Each formulation had at least 3 replicas. These were picked out periodically for weight measurements.

7. The soaked panels could dry for 3 days.

8. The soaked, dried coatings were measured for the dried weight, as compared to the initial weight (step 5).

ELISA

Protein adsorption was evaluated by Enzyme-Linked Immunosorbent Assay (ELISA) via measuring fibrinogen (Fg) adsorption:

1. Epoxy disks (1cm x1cm) were incubated in 1mL 1mg/ml Fg in a well plate for 90 min at room temp, followed by 5 washes with PBS buffer.

2. Samples were then incubated in 1 mL 1mg/ml bovine serum albumin solution for 90 min at room temp. They were again washed 5 times with PBS buffer. The panels were then removed and transferred to new wells.

3. They were next incubated with a 1:1000-dilution of horseradish peroxidase (HRP)-conjugated anti-fibrinogen in PBS for 30 min, followed by another 5 washes with PBS buffer.

4. The disks were removed after 5 washing, and transferred to new wells.

5. Finally, 500ul 1mg/ml o-phenylenediamine (OPD) in 0.1 M citrate-phosphate buffer, pH 5.0, containing 0.03% hydrogen peroxide, was added to each disk at 30-second intervals. The samples incubated in the OPD solution for 30 min and stored away from light.

6. The reaction was stopped by adding 500 ul 1N HCl. The supernatant was removed from each panel wells, transferred to a cuvatte, and its absorbance at 492nm was measured. All samples were measured in triplicates.

Gel Permeation Chromatography

Since we used a free radical method, molecular weight is characterized batch by batch to ensure that the performance of copolymer from each batch is the same.

Dynamic Scanning Calorimetry

DSC measures the thermal behavior of the polymers and sheds light on the behavior of the coatings. Depending on formulations, coatings could be stable or unstable with cracking. DSC helps to correlate the thermal behavior of the polymer with the coating behavior. Thus, DSC assists to optimize the coating formulations suitable for marine applications.

RESULTS AND DISCUSSION

Weight-loss study

The weight loss for the mixed-charge formulation was studied at the earlier part of this project. The results show that the self-polishing rate of the mixed-charge formulation is slow.

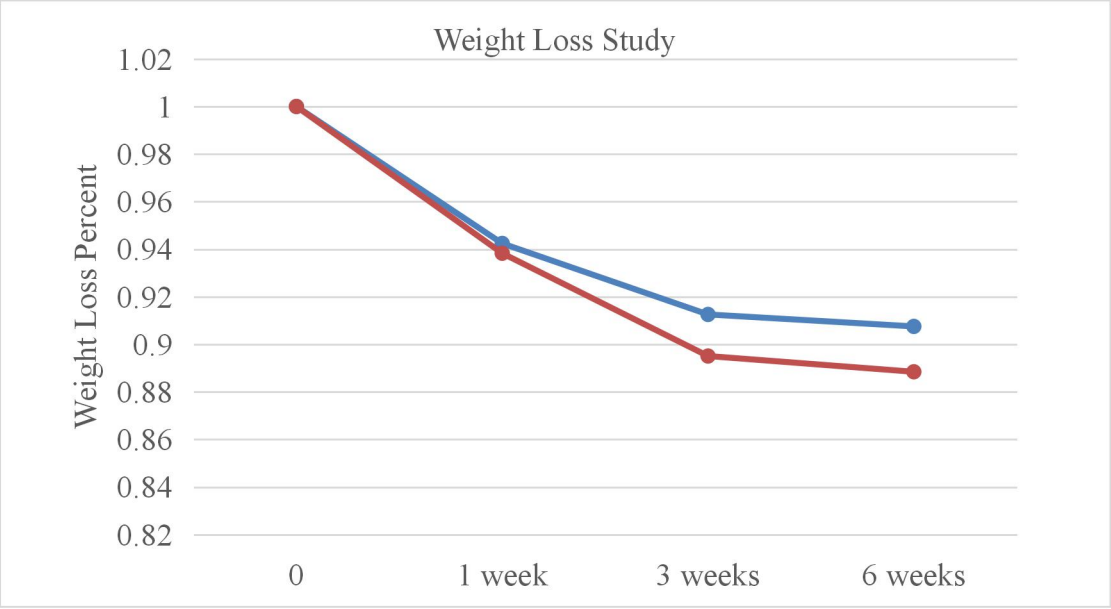

Fig. 5 Weight loss study for MC formulations 1 and 2

Fig.5 shows the results of two formulations with different counter ions (blue line is for lower counter ion while red line is for higher counter ion). As can be seen, the weight loss of the polymer coating and thus the self-polishing rate is faster with higher counter ions since counter ions introduce more hydrophilicity to the coating and increase the hydrolysis rate of the coatings.

It was also observed that the coatings showed varying degrees of opacity, swelling and hydrophilicity/hydrophobicity. Coatings with or without a crosslinker were also studied.

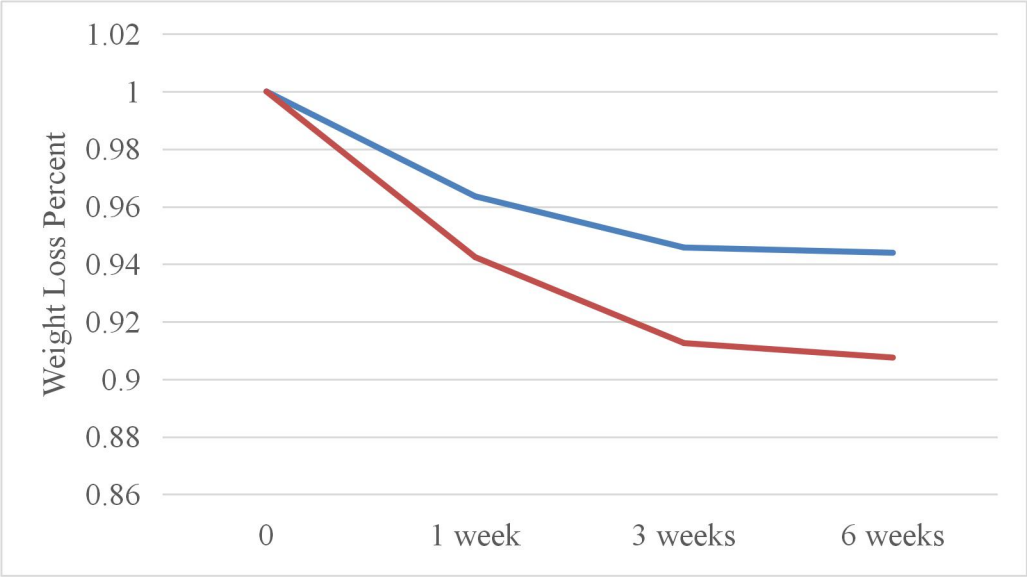

Fig.6 Weight loss study of MC formulations 1 and 4

From Fig. 6, it is clear that addition of crosslinker slows down the self-polishing rate. Depending on the amount of the crosslinker added, the hydrophobicity and swelling of the coatings can also be addressed. The chemical crosslinking provides three-dimensional crosslinking to the polymer coatings. Self-polishing is a process occurring at the interfaces. The addition of crosslinking provides one more dimension to the self-polishing process. Depending on the amount of crosslinking, the water penetration depth, hydrolysis of the polymer ester, and solubility of the hydrolyzed polymer were affected. Crosslinking increases the hydrophobicity of the coatings.

Different MC formulations studied are summarized in the table below.

Formulation	Hydrophobic 1	Hydrophobic 2	Mixed charge	Counter ion	Crosslinker
1	20	30	40	10	0
2	20	30	35	15	0
3	20	30	30	20	0
4	20	30	40	10	20%
5	20	30	35	15	20%
6	20	30	30	20	20%
7	20	30	50	0	0

Table. 1 Different MC formulations

Thermal Analysis

In order to identify formulations to be used, the thermal behavior of the polymers should be understood better, especially since the polymer changes its nature before and after hydrolysis. In addition, both crosslinker and counter ion could change the thermal behavior of the polymeric coatings as well. TGA and DSC experiments were performed to find the glass transition temperature of the copolymers. The TGA of homopolymers was taken from a reference. [19]

Results showed that the overall T_g of the polymeric coatings could be increased by adding a hard hydrophobic component. The pendant group of the hard compound could act as a barrier of the free rotation of the polymer chain, thus increasing the T_g of the polymer and the coating. This component also increased the hydrophobicity of the coating and reduced its swelling. Too much hard component could cause cracking of the coating due to increase in hardness. On the other hand, a soft component could reduce the T_g of the coating while keeping hydrophobicity. Due to the flexibility of the soft component with a lot of free chains, it increased the mobility of the chain and reduced the T_g of the coating.

The figures below give T_g for the hydrophilic compound and two of our formulations. For comparison of T_g among different formulations, it can be seen that glass transition temperature increases with the number of charged ion in the system.

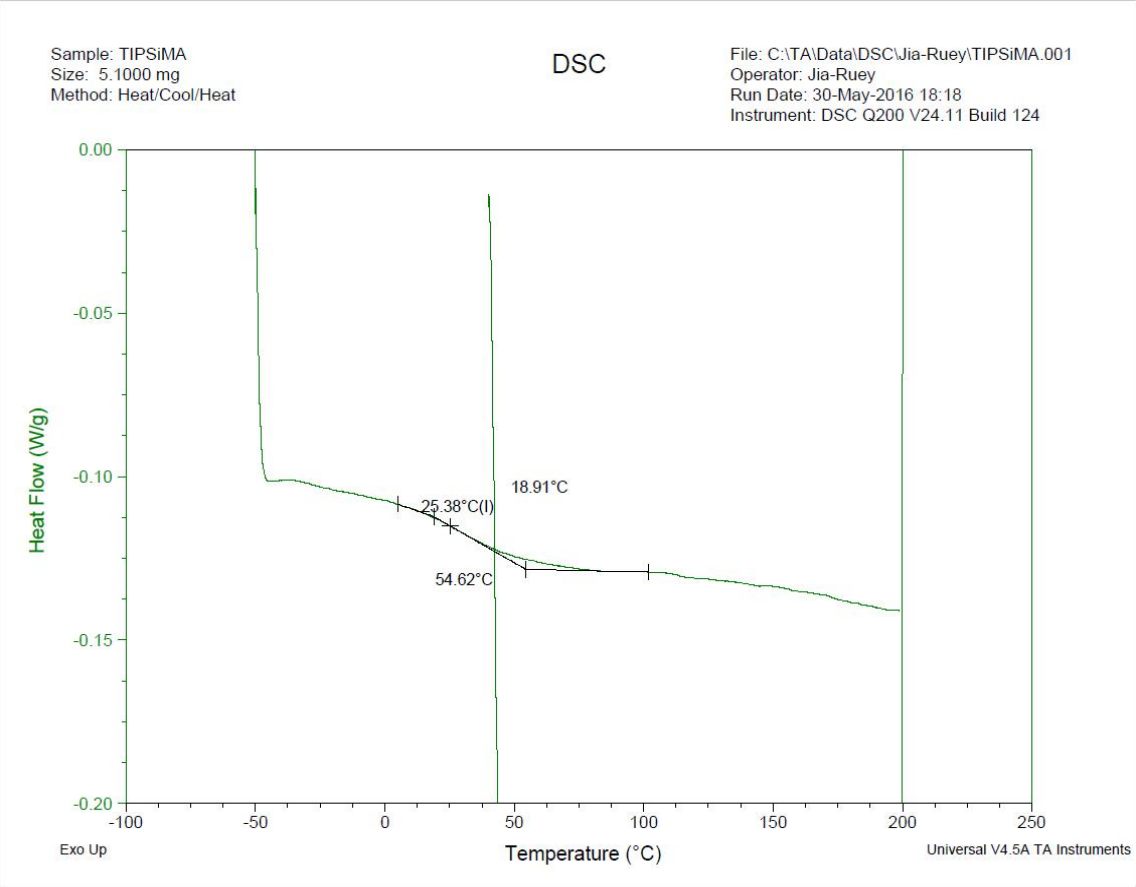

Fig.7 DSC for the hydrophilic compound

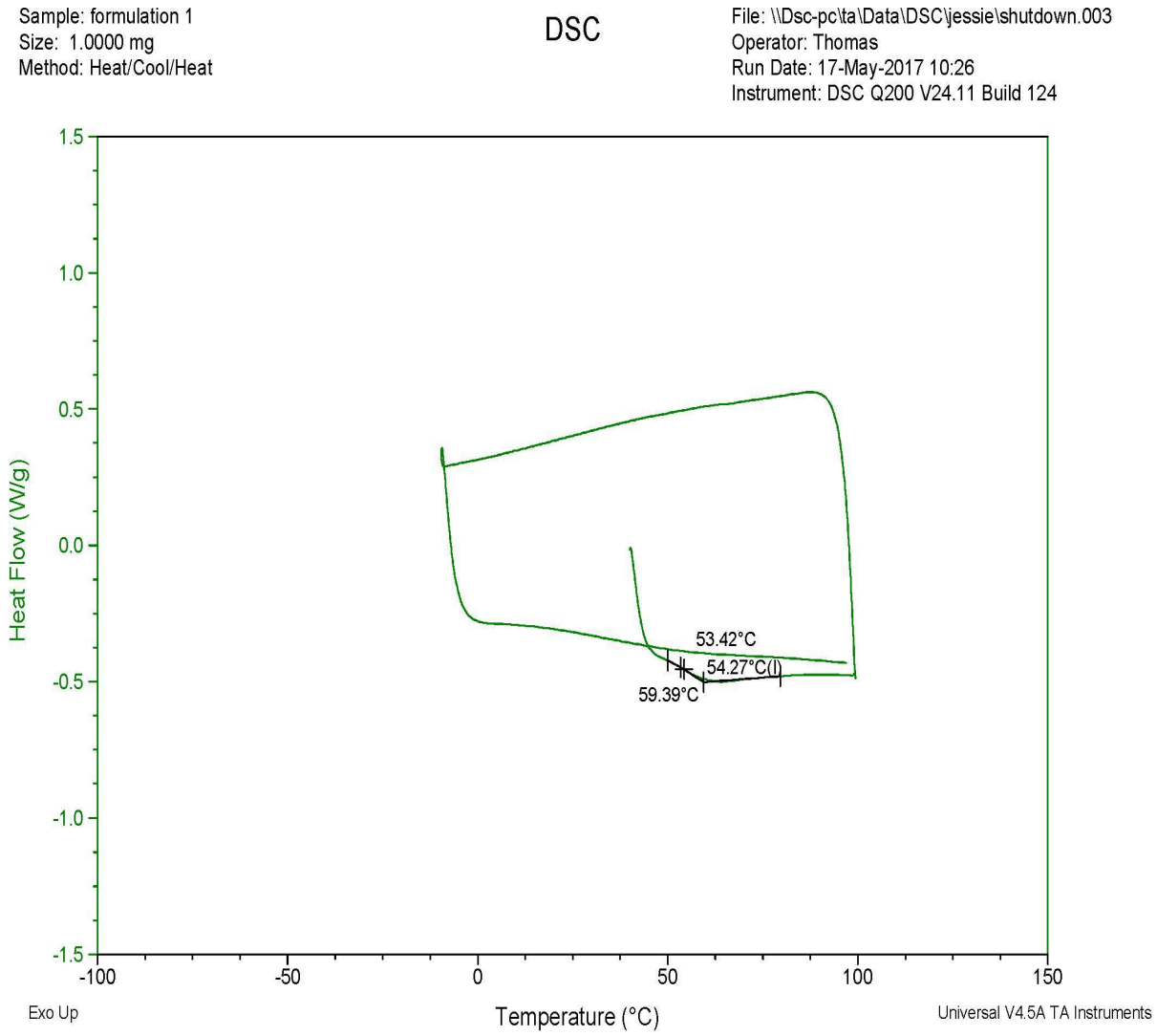

Fig. 8 DSC for MC formulation 3

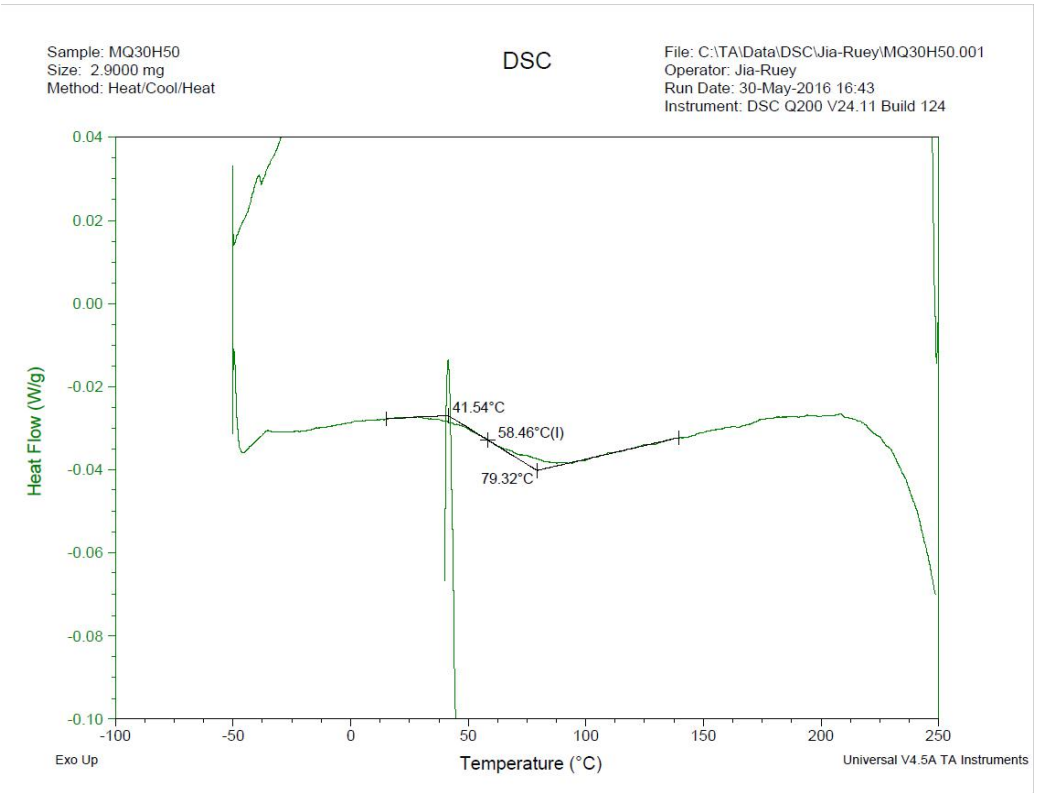

Fig. 9 DSC for the MC formulation 7

ELISA

To test the non-fouling behavior of our coatings, ELISA experiments were performed. Fibrinogen from human plasma was used as the foulant. It can be used as an indicative of the fouling level encountered in ocean. Protein adsorption is the first event for surface fouling, including in marine environment. Figure 11 shows ELISA results for one formulation.

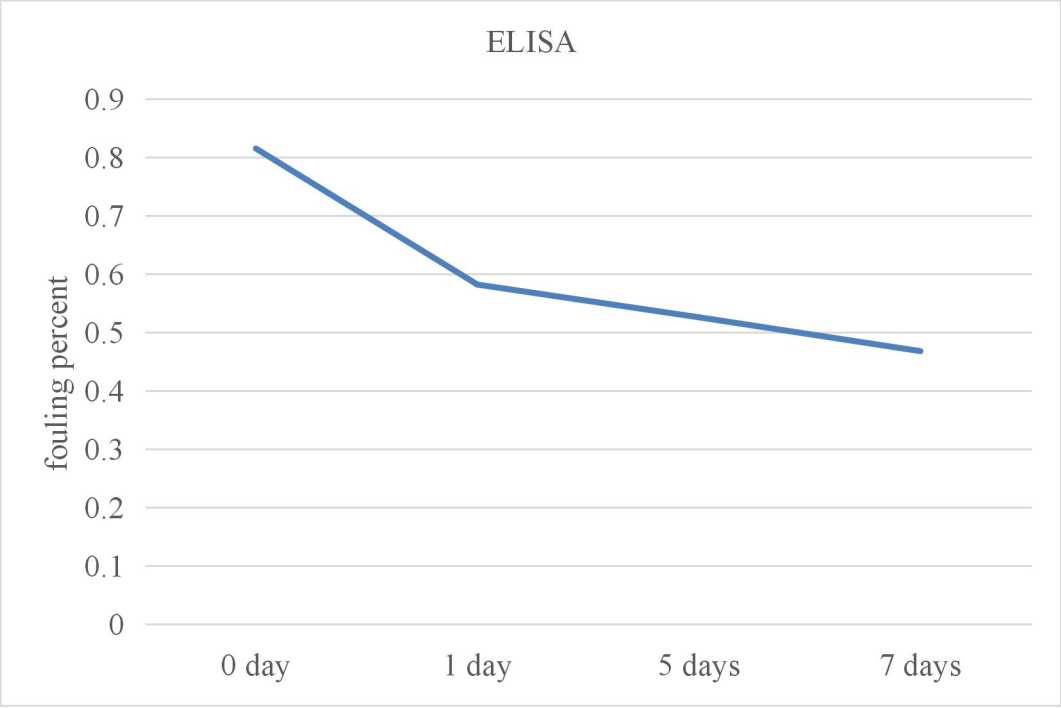

Fig. 10 ELISA for MC formulation 1

Fig. 10 is the measured adsorbed protein amount on a coating surface with respect to that at time 0 as a function of time upon soaking in seawater. The plot showed lower protein adsorption as the soaking time, indicating that self-polishing occurs. As mentioned earlier, the polymer is made of zwitterionic ester, which is hydrophobic at the beginning and becomes more hydrophilic upon hydrolysis. As expected, this surface coating has high fouling initially and lower as times go.

Copolymer weight

Gel permeation chromatography (GPC) was used to determine the molecular weight of the synthesized polymer. Figure 11 shows the molecular weight of a mixed-charge polymer (11 K) from GPC chromatogram. Figure 12 gives the standard equation used to calculate the molecular weight vs. retention time for the polystyrene standard.

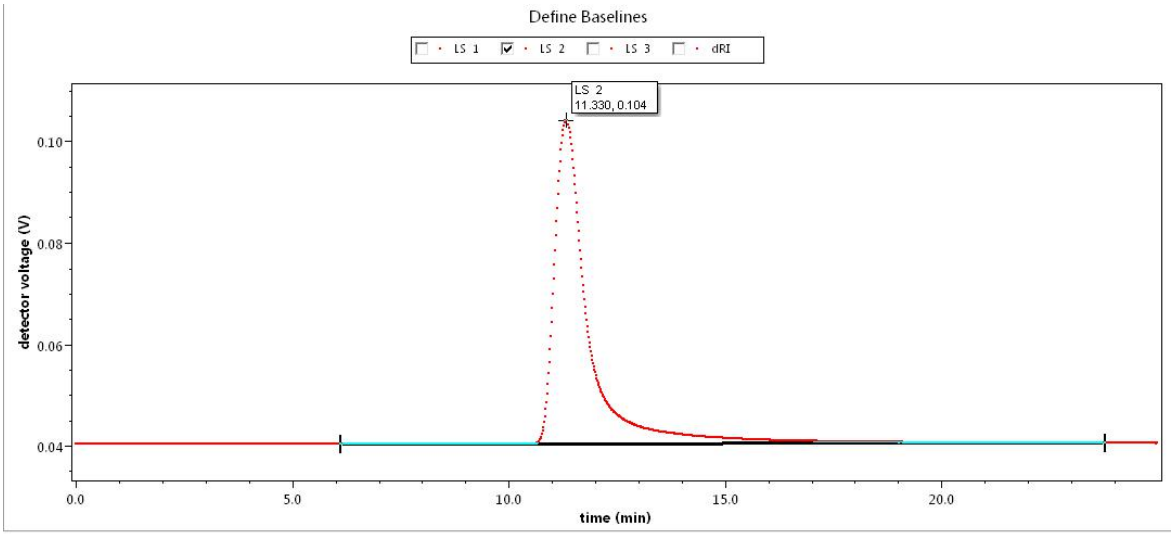

Fig. 11 GPC result for the MC formulation 7

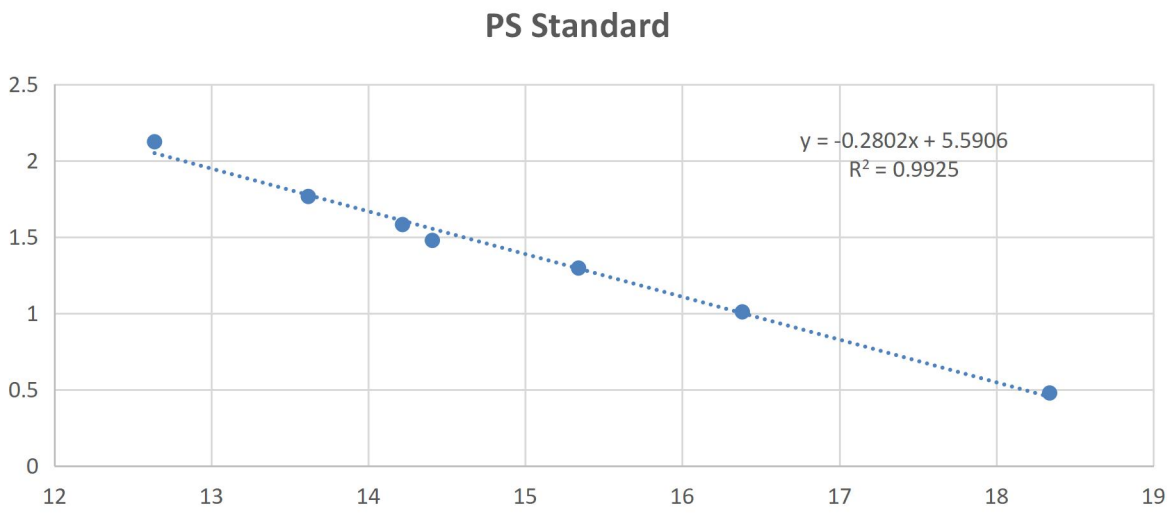

Fig. 12 Relationship between retention time and molecular weight

CONCLUSIONS

The results of weight loss study show that our coatings can hydrolyze after soaking in the artificial seawater. The results of ELISA study further show that our coatings can reduce protein adsorption upon hydrolysis. The ratio between hard and soft compounds and the amount of crosslinker can be adjusted to achieve good mechanical properties and to avoid cracking. These coatings will be tested in fields for their performance.

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