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Long-Term Stability of PEG-Based Antifouling Surfaces in a Marine Environment

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Abstract

The work presented here concerns the use of polyethylene glycol (PEG) to reduce marine biofouling on ship hulls. The long-term stability of PEG towards degradation in a marine environment is reviewed, and the results of experiments designed to test the degradation of polyethylene glycol moieties are disclosed. The results show how the degradation of different polyethers can be followed, both in laboratory accelerated conditions and real life exposure by size exclusion chromatography (SEC) and nuclear magnetic resonance spectroscopy (NMR). Preliminary results indicate the influence of the chemical structure and the end-group on the degradation of different PEG-containing compounds in accelerated conditions, while showing very little degradation in real exposure tests in seawater after 3 months. Further experiments will be discussed involving long-term stability and degradation pathways involved in the degradation of PEG.

Introduction

Biofouling is the accumulation of organisms on immersed surfaces, such as microbes, animals and plants [1, 2]. Biofouling in medical implants can lead to inflammatory, infectious, and thrombogenic problems [3, 4]. In seawater, ships can suffer from marine biofouling on their hulls. This results in higher frictional resistance, lower maneuverability and increased dry docking time, with the consequent increase in operational costs [1]. Polyethylene glycol (PEG) is commonly applied to combat fouling both in the biomedical industry [4, 5] and in antifouling coatings for ship hulls [2]. For PEG to be a viable long-term solution on ocean going vessels, it needs to satisfy the stability criteria of an antifouling coating. That is, it needs to be effective, retained or replenished on the coating surface and stable in the marine environment. This paper concerns the latter, namely the stability of PEG oligomers and polymers when exposed to natural seawater.

Polyethylene glycol

Polyethylene glycol, also known as polyethylene oxide (PEO), is a linear, crystalline, non-ionic and thermoplastic polymer with chemical structure $[\text{CH}_2\text{-CH}_2\text{-O}]$ [3, 4]. PEO has the unusual property of being soluble in water from short oligomers up to polymers with some millions of molecular weight (MW) [3, 4, 6]. It has been suggested that the chemical structure of PEG, allowing high degree of polymer-water interaction via hydrogen bonding, could be the reason for the high degree of solubility in water. In this model, 2 or 3 water molecules are bonded to each PEG unit [4].

Antifouling effect of PEG

The presence of PEG moieties on different surfaces in aqueous media has demonstrated both a decrease in frictional response to shear [7] and a clear resistance to nonspecific protein and cell adsorption, reducing the amount of fouling on those surfaces and making PEG very attractive for biomedical applications [4, 5]. Different properties of PEG have been pointed as crucial for its antifouling performance [4, 5]: the hydrophilicity, the high mobility and the conformation of the chains, its neutral charge, and the hydrogen bonding capability.

The antifouling mechanisms of PEG that have been proposed can be summarized in four main points [4, 5]:

(1) Low interfacial free energy. The hydrophilic nature of PEG reduces the water-surface interfacial energy, thus decreasing the driving force for nonspecific protein adsorption.

(2) Steric stabilization. The presence of a protein approaching a surface with PEG moieties would reduce the amount of conformations available of the PEG chains. At the same time, the protein would displace some water bonded to the PEG units, which would change the polymer-water solvation state. Both phenomena would increase the free energy of the system, so the process is not favourable and the protein is kept off the surface.

(3) Chain mobility. The high mobility of the PEG chains are suggested to shorten the contact time of the protein on the surface, therefore decreasing the amount adsorbed.

(4) Bound water shell structure. The hydrogen bonding of water molecules around the PEG chains creates a kind of shell of ordered water that will act as a barrier to approaching proteins.

The functionalization of surfaces with PEG groups has been achieved by different techniques: bulk modification of the immersed material, adsorption of PEG, covalent grafting, use of PEG-containing block copolymers as additives, etc. [4].

Irrespective of the method, the length and density required to achieve an optimal configuration has been investigated extensively, as well as the influence of the end-group [5]. However, with contradicting results.

Stability of PEG

PEG has poor stability under a range of conditions due to different degradation mechanisms, both biotic and abiotic. The degradation of PEG has been suggested as one of the possible reasons for the failure of PEG surfaces in long-term experiments [5, 8].

Han et al. [9] concluded that PEG6000 is degraded by thermal oxidation at 80°C in the presence of oxygen. They reported that both the removal of oxygen and the use of an antioxidant effectively suppress the degradation of PEG. Branch et al. [8] also found thermal oxidative degradation taking place at 37°C in aqueous solutions.

The biodegradation of PEG in both aerobic and anaerobic conditions has been demonstrated with MW up to 20000 by using sludge microbes, with higher degradation rates in aerobic conditions [10]. Schink et al. [11] degraded PEG of chain length up to 20000 in MW by anaerobic bacteria. Schramm et al. [12] showed bacterial degradation of PEG in anaerobic conditions. Low MW PEG and polypropylene glycol (PPG) have also been biodegraded in river water [13], while Herold et al. [14] used alcohol dehydrogenase (ADH) for the aerobic enzymatic degradation of low MW PEG. Haines et al. [15] and Kawai et al. [16] showed microbial degradation of PEG up to MW of 10000 too.

Finally the presence of transition metal ions have proved to oxidize PEG in the presence of oxygen [5,17]. This is in agreement with the Fenton reaction [18], where the presence of iron, oxygen and hydroxyl radicals oxidize the PEG chains.

In spite of the extensive research in this topic, most of the reported studies have been on the degradation of PEG in air or in freshwater, while very little literature is available on PEG degradation in seawater [19]. Bernhard et al. [19] compared the microbial degradation of PEG in seawater and wastewater and reported important differences, both in terms of biodegradability and biodegradation rates.

In the case of biotic degradation, different mechanisms have been proposed. While the most accepted mechanism is oxidation of the PEG chain [12, 13, 16, 19, 20], some others defend that PEG can be degraded by hydrolysis [15, 20] or by a combination of both [17].

The chemical pathway of PEG degradation is not fully understood. The most accepted pathway involves the oxidation of the terminal hydroxyl group to aldehyde and carboxylic acid, followed by the cleavage of the ether bond and thus reducing by one unit the length of the chain as shown in Figure 1 [16, 19]. In this scenario, the end-group of the PEG chain will be a key factor determining the stability of the polymer. Others have suggested a random chain scission oxidation mechanism, leading to shorter homologues [9, 17], analogue to the pathway in thermal/oxidative degradation of PEG [21], thus suggesting that the chemistry of the end-group is not an important parameter in the biodegradation of PEG. It has been furthermore suggested that the pathway may depend on the MW of the polymer [19].

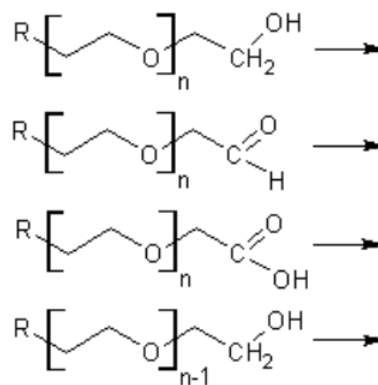


Figure 1: Oxidation pathway of PEG [16].

Experimental

Two different set of experiments were undertaken to assess the degradation of different compounds containing PEG (see compounds A-E in Table 1).

First, compounds A-E were exposed to different degrading agents in the lab in accelerated conditions. Such agents are UV-light, hydrogen peroxide (H₂O₂), temperature and transition metals, both in freshwater and seawater taken from the Baltic Sea (near Copenhagen). After exposure, the chemicals A-E were isolated and analysed by size exclusion chromatography (SEC) and Nuclear Magnetic Resonance spectroscopy (NMR). Moreover, some glass surfaces functionalized with PEG moieties were also exposed to the aforementioned agents and analysed.

Secondly, compounds C-E, PEG-containing copolymers, were used as additives in conventional polydimethylsiloxane (PDMS) coatings. These coatings were prepared by mixing an OH terminated PDMS of MW = 40000 g/mol with a trifunctional oximosilane crosslinker in the presence of xylene as solvent. Copolymers C, D and E were added so they accounted for 3% of the total weight of the dry film. The mixtures were applied on PMMA substrates with a wet thickness of 300 μm and they cured at room temperature for 3 days. After curing, the coatings were immersed in the sea in two different locations (Barcelona and Singapore) for different periods. After retrieval, the coatings were immersed in tetrahydrofuran (THF) for 5 hours to extract the additives from the coating. Then the THF samples were run in a semi-preparative SEC column and the fractions corresponding to the copolymers were fractionated, for further NMR and SEC analysis.

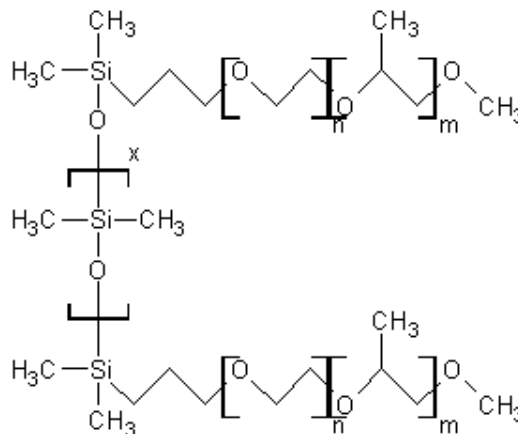


Figure 2: Chemical structure of Copolymer C.

Table 1: PEG-containing compounds

Compounds	Chemical structure	End-group	PEG:PPG ratio ^a
A	Homopolymer PEG	OH	1:0
B	Copolymer PEG-b-PPG-b-PEG	OH	1:2
C	Copolymer (PPG-co-PEG)-b-PDMS-b-(PEG-co-PPG)	OCH ₃	3:4
D	Copolymer PDMS-g-(PEG-co-PPG)	OCH ₃	9:4
E	Copolymer PDMS-g-PEG	OCOCH ₃	1:0

^a weight ratio

Results and Discussion

The preliminary results of the accelerated tests (not shown here) show how the difference in chemical structure and the degrading conditions have an influence on the degradation results. However, the results show some uncertainties that will be discussed and future steps will be considered.

Figure 3 shows the results of compounds C-E that have been exposed in seawater as additives in PDMS coatings. The PEG and PEG-co-PPG chains do not suffer degradation after 3 months of exposure in Singapore. There is an increment in the amount of PDMS (results not shown) in the results compared to the original C-E compounds, as well as an apparent increase in the number of PEG units per chain for copolymer

E. Both increments will be addressed in the presentation. It will show furthermore the results obtained after exposing compounds C-E 2 years in seawater in Singapore and 5 years in Spain, which will show how the degradation depends on the PEG/PPG structure as well as the presence of other compounds in the PDMS matrix.

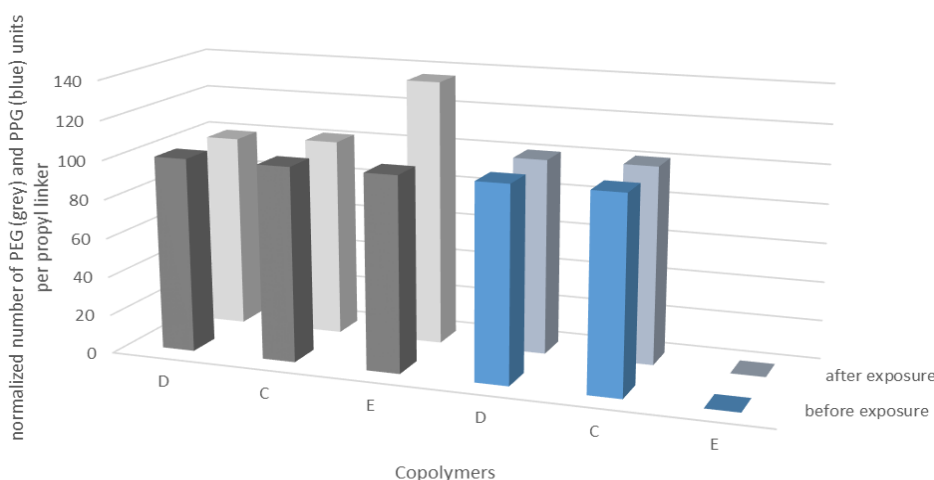


Figure 3: Normalized number of PEG (grey, left) and PPG (blue, right) units per each propyl linker for copolymers C, D and E, before and after exposure (3 months) in seawater in Singapore.

Conclusions

- This paper reveals a method to monitor the degradation of different polyethers, both in laboratory accelerated conditions and real life exposure by SEC and NMR.
- Preliminary results show that, PEG-containing compounds used as additives in PDMS coatings suffer very little degradation, if any, over 3 months of seawater exposure in Singapore.
- Further experiments are required in order to follow the polyethers degradation over longer time and the degradation pathway involved.

Acknowledgements

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