Journal of Polymer Science & Applications

Editorial

A SCITECHNOL JOURNAL

The Challenge of Non Fouling Surfaces: Polymers could be the Answer

Elena Vassileva*

The immersion of engineered materials in water environment such as sea water, industrial waters (heat exchangers, pipes), body fluids, etc., is always accompanied by an accumulation and colonization of their surfaces with biological matter and water born organism (e.g. bacteria, barnacles, algae, etc.). This process, known as biofouling, affects detrimentally the materials and related devices performance in many applications. For example, biofouling of ship hulls causes reduction in the ship speed and increases the fuel consumption up to ~ 40% more as compared to the non-fouled vehicles [1]. Moreover, the greenhouse gas production increases and the formed biofilms spread the water born organism around the world – a process that could destroy the balance in sensitive ecosystems. Biofouling on measuring instruments used in sea, oceans and on the coast could significantly affect the data quality and the instrument performance [1].

The biofouling generates also problems in industrial applications, such as e.g. heat exchangers, where due to the biofilm formation the heat transfer rate is reduced by 20 to 50%. This results into an increase in the global expenditure to control the problem with ~ $15 billion per annum [1]. The biofouling is the primary limitation for widening the application of membrane technology, microfiltration and ultrafiltration membranes for drinking water production and wastewater treatment. The reason is that the formed biofilms significantly reduce the permeating flux, increase the energy consumption, and could result in contamination of filtrated water.

Biofouling is a huge problem for the biomedical implants and devices as well [2]. The biological fluids are rich in proteins, cells, etc., and they also could be contaminated by pathogens. All these species could strongly adhere onto the biomaterials surfaces, initiating biofouling and changing drastically the original surfaces characteristics, deteriorating in this way the biomaterials performance. For example, the microbial colonization of catheters often results into urinary tract infections which makes the latter the most common hospital-acquired infections [3]. Other bio-devices, which could be adversely impacted by biofouling, are prosthetic implants, biosensors, dental implants and medical equipment. The non-desired biofouling could result into implant rejection, malfunction of biosensors and spread of infectious diseases [4].

Two main strategies are used now-a-days for fighting biofouling, namely: (i) bioactive compounds release and (ii) surface chemistry/micro topography modification. The first one takes advantage of small molecules with e.g. biocide activity, which are released in the environment, while the second one consists in biomaterials surface modification, e.g. through making use of non-fouling polymers and related materials (physico-chemical approach) and/or by imparting an appropriate topography of the surface (physical approach). Both strategies are in fact taken from nature, as these are the natural ways for fighting/preventing biofouling. Many marine organisms, including sharks, skates, and rays, have specific topography on their skins – placoid scales, known as dermal denticles. The latter consist of a vascular core from dentine surrounded by an acellular "enamel" layer, similar to the human teeth [4]. Besides the purely mechanical functions of these denticles, as e.g. reduction of mechanical abrasion and of the hydrodynamic drag, this specific topography protects the marine organisms from ectoparasites. Similarly, a combination of grooves and ridges is a way to prevent in short terms the biofouling on e.g. dolphin and whale skins, mussels shells, etc [4]. The long term natural antifouling, however, is a combination of surface chemistry and micro topography.

The biofouling of implants and devices in living organisms starts with the protein adhesion on the biomaterials surfaces – a process which takes place extremely rapidly within the first seconds to minutes after the implant/devise immersion in the body. The change in the conformation of the adhered proteins is crucial for the further biofouling proceeding as it is the one that could trigger the cells (e.g. macrophages) attachment. The attached macrophages fuse and form the giant cells, starting to release at the same time inflammatory cytokines. These cascades of reactions are part of the foreign body reaction that usually takes place when foreign body is introduced into mammals. The final result is the formation of a dense fibrous capsule, impermeable or hypopermeable, around the implant or device implanted *in vivo* into the mammals which isolates it from the rest of the body and hampers its final performance. The foreign body response is difficult to overcome and although many different biomaterials have been tested, still the creation of a stealth material that circumvents the ability of the mammalian surveillance systems to distinguish foreign from self is a big challenge [5].

The foreign body reaction's initial cascade of processes is very similar to the onset of the bacterial biofilm formation, where the formed protein layer could act as a conditioning film for the settlement of bacteria and microorganisms. The bacterial biofilms impose serious problems because they are highly resistant to antibiotics and antibacterial agents as compared to the single bacteria due to bacteria communication within the biofilm (quorum sensing). Thus many attempts are under way now-a-days for creating antifouling and antibacterial coatings as the burden of bacterial biofilms is enormous.

It is now well known that the protein adsorption, i.e. the first stage in these two different examples of biofouling, strongly depends on the biomaterials surface characteristics, such as the physical and chemical properties of the surface, as well as its electrostatic charge. The protein adsorption and respectively protein denaturation is strongly defined by the chemistry of the surfaces. In a recent study, Whitesides and coworkers have defined the main characteristics of non-fouling surfaces [6]: they should be hydrophilic, electrically neutral, should contain hydrogen bond acceptors but not hydrogen-bond donors.

***Corresponding author:** Elena Vassileva, Laboratory on Structure and Properties of Polymers, Faculty of Chemistry and Pharmacy, Sofia University, Sofia, Bulgaria, Tel: (+359 2) 8161 614; E-mail: ohtev@chem.uni-sofia.bg

Received: March 27, 2017 **Accepted:** March 28, 2017 **Published:** March 31, 2017

According to another theory, the non-fouling materials have very low surface energy expressed as Critical Surface Tension, CST [7]. Thus, all surfaces that have CST between 20 and 30 mN/m are non-fouling. Many researchers have recognized the important role of water for imparting non fouling behavior. The existence of bound and unbound (free) water is frequently used for explaining the observed non fouling materials performance.

All theories, developed until now for explanation of the non-fouling behavior of materials, however, recognize that the *surface chemistry* is the main factor for the formation, stability, and release of the adhered fouling organisms to the materials surfaces.

Since long time poly (ethylene glycol)(PEG) and PEG based materials are widely recognized as the golden standard in the field of surfaces/materials that exhibit high resistance to protein adsorption and biofouling. The mechanism behind is the steric repulsion between the PEG chains which arises when the protein approaches the PEG containing surface. In fact, the approaching proteins collide with PEG surface thus causing removal of the water molecules form the swollen PEG layer. In this way, a loss of entropy occurs – PEG chains are more compressed and more immobile as a result from the water loss. Steric repulsions between the protein and the PEG take place and the proteins do not adhere on the surface. In spite of the very good non fouling performance, however, PEG is susceptible to oxidation, which limits its long-term *in vivo* applications. Moreover, it is unable to prevent the foreign body reaction's fibrous capsule formation.

The role of water for the non-fouling properties of many surfaces is widely recognized. Many studies showed that the increase in the hydrophilicity of the surfaces suppress the protein adhesion and respectively prevents the cell attachment. Thus hydrogels – polymer networks that swell in water - are often used as non-fouling materials/surfaces. Many hydrophilic polymers networks of e.g. poly (vinyl alcohol), poly (2-hydroxyethyl methacrylate) (PHEMA), crosslinked PEG diacrylate are proved to be non-adhesive for many bacteria. Surfaces that are more hydrophilic, as established by e.g. the contact angle measurements, exhibit lower protein adsorption. The hydrogel's non fouling behavior well corresponds to the above mentioned relation between the relative adhesion of fouling organisms and the surface energy CST. This relation admits, however, not only hydrophilic but also hydrophobic surfaces/polymers to exhibit non fouling activity, e.g. to be thrombo resistant. For example, among the three hydrophobic polymers: polydimethylsiloxane, polytetrafluroethylene and polyethylene, only PDMS is found to be thrombo resistant [7] and this is explained by the fact thatit is the only one among the three which has CST value between 20 and 30 mN/m, i.e. corresponds to the CST values defining non fouling behavior.

Thus, the three theories are mutually related but neither one of them is able to fully explain the non-fouling behavior of materials. However, the three of them acknowledge the key role of the surface/materials chemistry for imparting non fouling behavior.

Recently a great interest among the researchers has raised the zwitterionic structures and in particular zwitterionic polymers. Zwitterionic compounds possess in their structure covalently bonded positive and negative charges, although as a whole their molecules remain electrically neutral. The poly zwitterions are regarded as structural analogs to several natural motifs, e.g. the betaine structure of aminoacids, the phosphorylcholine zwitterionic head, the RGD moiety, etc. They are the first class of polymers proved to be effective in the mitigation of the foreign-body reaction [8]. Poly (carboxybetaine methacrylate), which is an exact structural analog of the glycine betaine, strongly resists the formation of a collagenous capsule in a mouse model. Moreover, it facilitated them to micro vessel formation in the surrounding tissue which is highly desired for a broad spectrum of *in vivo* applications and thus offer the potential to improve the performance of current medical devices, such as glucose sensors and drug-releasing devices, tissue scaffolds and artificial organs, where fibrotic reactions are undesirable.

In addition, recent studies have shown that PZI possess antibacterial activity, prevent the biofilm formation, and thus show a great potential for all non-fouling related applications, including as well an antifouling performance in marine environment [9].

The challenge for non biofouling behavior of the materials and devises, used in water environment, still remains and that is why many researchers from different disciplines work on it in many different fields of applications. Despite the different approaches used, the polymers are the key players for its successful solution as they provide a combination of an appropriate surface chemistry and possibility for controlled surface micro topography, as learned from the nature lessons. Zwitterionic polymers are the rising star in the field but as the challenge is huge, another serious competitor could be expected soon.

References

1. AMBIO project: http://www.birmingham.ac.uk/generic/ambio/index.aspx
2. LM Hamming, PB Messer smith. (2008) Fouling Resistant Biomimetic Poly(Ethylene Glycol) Based Grafted Polymer Coatings. Material Matters 3: 52.
3. J Brosnahan, A Jull, C Tracy (2004) The Cochrane Database of Systematic Reviews Art. CD004013.
4. Magin CM, Cooper SP, Brennan AB (2010) Non-toxic antifouling strategies. Mater Today 13: 36-44.
5. Ward WK (2008) A Review of the Foreign-body Response to Subcutaneously-implanted Devices: The Role of Macrophages and Cytokines in Biofouling and Fibrosis. J Diabetes Sci Technol 2: 768-777.
6. Ostuni E, Chapman RG, Holmlin RE, Takayama S, Whitesides GM (2001) A Survey of Structure-Property Relationships of Surfaces that Resist the Adsorption of Protein. Langmuir 17: 5605-5620.
7. Baier RE (2006) Surface behaviour of biomaterials: The theta surfacefor biocompatibility. J Mater Sci.: Mater Med 17: 1057-1062.
8. Zhang L, Cao Z, Bai T, Carr L, Ella-Menye JR, et al. (2013) Zwitterionic hydrogels implanted in mice resist the foreign-body reaction. Nature Biotechnol 31: 553-556.
9. Quintana R, Jańczewski D, Vasantha VA, Jana S, Siew S, et al. (2014) Sulfobetaine-based polymer brushes in marine environment: Is there an effect of the polymerizable group on the antifouling performance? Colloids Surf B Biointerfaces 120: 118-124.

Author Affiliation Top

Laboratory on Structure and Properties of Polymers, Faculty of Chemistry and Pharmacy, Sofia University, Bulgaria