

POLYMERS AT INTERFACES: BIOLOGICAL AND NON-BIOLOGICAL APPLICATIONS

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Abstract

Polymer is a long chain macromolecule comprising of several monomers. The interface is the dividing region between two phases. In this article the authors describe about the polymers at interfaces. The interfacial behaviour of polymers is an area of active research and holds immense potential for technological advances. Polymers can adhere to an interface either by physisorption or by chemical grafting. This article discusses and summarizes important work in the literature regarding the various technological applications of polymers at interfaces. They are explored cutting across disciplines and emphasizing the versatility of the interfacial behavior phenomenon. The fields of colloidal stabilization and bridging flocculation, detergency and biomedical applications are explored and latest developments in these areas are focused. The emphasis is on practical issues rather than on the theoretical ones, as there are quite a few review articles available on the latter. This article will be a valuable source of information for the researchers who are starting their career in polymers related to biotechnology and chemical engineering.

Keywords: Polymer adsorption, Colloidal stabilization, Bridging flocculation, Detergency, Biomedical applications

Introduction

Polymeric solids and polymer solutions have been well studied in the past. Indeed these fields are well established and have revolutionized all fields of science and technology. The interfacial behavior of polymers is a relatively young field and an area of cutting edge research. The impetus for this research activity is provided by the manifold extant and emerging applications of polymers at interfaces. The applications cut across disciplines and provide a fertile meeting ground for chemists, chemical engineers, material scientists, physicists, biologists and others.

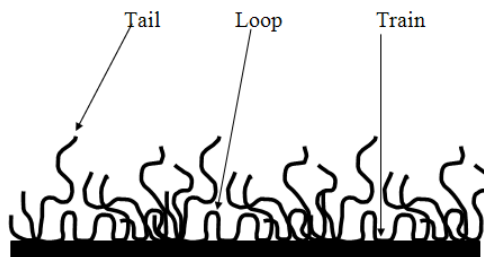
Several excellent reviews have appeared in the recent past bearing on the scientific aspects of interfacial behavior of polymers. A comprehensive review of physical characterization and theoretical analysis of polymers at interfaces was reported¹. Moreover various theoretical issues related to the adsorption of neutral and charged polymers at equilibrium were also discussed². A survey of current research directions concerning the structure, dynamics and interfacial activity of polymers with special emphasis on nanoscale research was also presented³. The status of theoretical models describing the interfacial behavior of polyelectrolytes was efficiently explained⁴. It is evident that research in this field is in a state of active growth and development. Applications of

polymers at interfaces are multifarious and it is the objective of this review article to illustrate this diversity and complexity to researchers of different backgrounds and specializations.

Types of Polymer Interfacial Behavior

Polymers can attach to interfaces through physisorption or chemisorption (end-tethering)¹. Physisorption or physical adsorption of polymers is different from small molecule physisorption. Small molecules attach themselves at one site only. Polymers, being long chained, can attach at multiple sites resulting in what is called the train-loop-tail structure (Fig1).

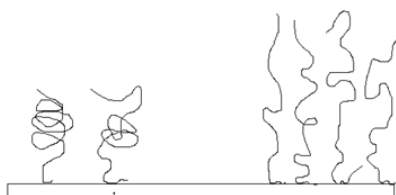
Fig 1: Train-loop-tail model of polymer adsorption



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While physisorption is a reversible phenomenon in the case of small molecules, the probability of detachment of a polymer chain from all attached sites at the same time is very small and hence polymer physisorption is considered irreversible for all practical purposes. Chemisorption is the formation of a chemical bond between adsorbate and adsorbent and, in the case of polymer chemisorption, results in end-tethered or covalently grafted polymer chains. Depending on the graft density, the polymer chain can exist in mushroom structure (Low graft density) or brush structure (High graft density) as reported by the researchers⁵⁻⁶ and as shown below (Fig 2).

Fig 2: States of tethered chains: Mushroom (right) and brush (left)



Both physisorption and end-tethering have their own role to play in practical applications. When a strong attachment to the surface is needed, end-tethering may prove viable but when a cheap technique is needed, physisorption may be used since it is less process-intensive. In what follows, we will explore the practical areas in which these phenomena find applications.

Colloidal Stabilization

Colloidal systems are dispersions of a finely divided phase in a dispersion medium. In most common colloidal systems, the continuous phase (Dispersion medium) is a liquid. When the subdivided phase is a solid, the dispersion is called a *sol* and when it is a liquid it is called an *emulsion*. In a colloidal system, the size of the colloidal particle ranges from 1nm to 1 μ m⁷.

Colloidal particles in a dispersion medium exhibit brownian motion and hence collide with each other frequently. Upon such collision, they may experience an attraction and adhere together resulting in floc formation (Flocculation) thereby destabilizing (Coalescing) the colloidal system. If the colloidal particles repel each other the system will be stable and remain in a dispersed state. In several situations as in the case of paints, we desire the colloidal dispersion to be stable.

Van der Waals forces (Primarily London or dispersion forces) are the primary sources of attraction between colloidal particles. In many colloidal systems, the range of the van der Waals forces is 5-10 nm.

Therefore the need is to provide a long range repulsion (~ 10 nm) between the particles so to impart stability. This repulsion should be at least as strong as the attractive force and comparable in the range of the attractive interaction. Stability of the colloidal dispersion can be obtained by surrounding the colloidal particle with an electrical double layer (electrostatic or charge stabilization). It is also done with physisorbed or end-tethered polymeric molecules (steric stabilization). Moreover it can be also done with free polymer in the dispersion medium. Combination of the first two stabilization mechanisms leads to electrosteric stabilization. We will focus on steric and electrosteric stabilization since these approaches rely on the interfacial behaviour of polymers.

Steric stabilization

Steric stabilization of colloidal particles is achieved by grafting or physisorption of macromolecules to the surface of the particles⁸.

Fig 3: Steric stabilization



The repulsion between the two steric stabilized colloidal particles is entropic in nature. When the adsorbed layers come close, the segments present in the interaction region lose configurational entropy. That is, the polymer segments occupy fewer possible configurations in the compressed state than in the uncompressed state. This reduction in entropy increases free energy, producing the net effect of repulsion between the particles.

Several significant strides have been taken in the field of steric stabilization. Some researchers⁹⁻¹¹ focused on the stabilization of titania particles in particular due to their use in paints. Studies were made on adsorption of pluronics on poly-(D,L -lactic-co-glycolic acid) nanoparticles. Polymeric surfactants have also been reviewed by researchers¹²⁻¹³ and it was observed that such polymers can be used not only to stabilize sols but also emulsions. For instance, Chausson et al¹⁴ have used block copolymers poly (caprolactone)-b-poly(ethylene oxide) for stabilization of emulsions and suggested that they have promise in stabilizing nanoemulsions. The attraction of poly (caprolactone) is its biocompatibility and biodegradability. The stabilization/ destabilization of triglyceride emulsions by globular proteins was reviewed¹⁵. Similarly, Khristov and Czarnecki¹⁶ have reviewed polymeric stabilization of water/oil/ water

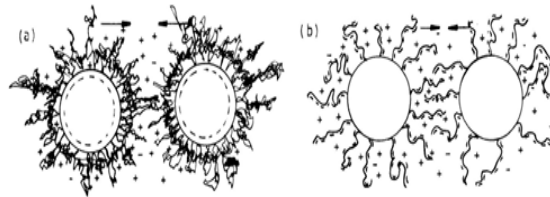
(w/o/w) and oil/water/oil (o/w/o) emulsion films. Stabilization of bubbles and foams have also been reported¹⁷.

Other novelties include the stabilization of colloids in supercritical CO₂¹⁸ and stabilization of nanosuspensions¹⁹. On the theoretical front, the computer simulation of steric stabilization with particular reference to the Vrij-Asakura-Oosawa model was also studied²⁰.

Electrosteric stabilization

In this form of stabilization, both steric and electrosteric repulsion combines to stabilize the dispersion. The origin of the electrosteric component may be a net charge on the particle surface (Fig 4a) and/or charges on the polymer attached to the surface (i.e. through an attached polyelectrolyte) (Fig 4b).

Fig 4: Schematics of electrosteric stabilization: (a) Charged particles with nonionic polymers. (b) Polyelectrolytes attached to uncharged particles



Several works in the recent past have dealt with electrosteric stabilization. It was suggested²¹ to use comb polyelectrolytes to stabilize alumina colloidal particles in electroless nickel solutions. Reports were made regarding the adsorption of biopolymers, especially proteins, for stabilization of colloidal particles²². The stabilization of concentrated cement suspensions using an anionic "superplasticizer" (Melamine formaldehyde sulfonate) was described²³. Affixing polyelectrolytes to polymer particles via photoemulsion polymerization was also discussed²⁴.

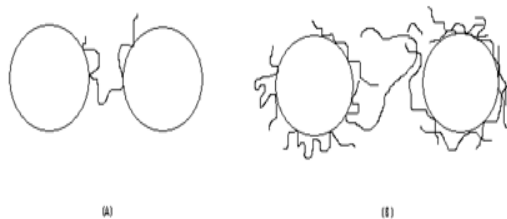
Flocculation and waste water treatment

In several cases, such as in waste water treatment, it is desirable to destabilize the colloidal system and bring about flocculation rather than stabilizing it²⁵. For

this purpose, hydrolysable metal cations such as alum, lime, ferrous sulphate and ferric chloride are commonly used as coagulants²⁶. The disadvantages of inorganic coagulants are the high dosage required, tight pH control, and the generation of excessive amounts of phyto-toxic sludge that cannot be disposed off easily²⁶⁻²⁸.

Polymeric materials can be used as flocculants as well. Such polymers act by forming a bridge between the colloidal particles and the process is called bridging flocculation²⁹. Colloidal particles can flocculate by the bridging mechanism in two ways. The first way is by bridging of the particles by one polymer molecule attached to both particles (Fig 5a) and second is bridging by the interaction of polymer chains attached to different particles (Fig.5b).

Fig 5: Schematics of bridging flocculation: (a) Two particles by one polymer molecule, (b) Two particles by two separately adsorbed polymer molecules



There are many advantages of using polymer flocculants^{27-28, 30}. The first and foremost advantage is that though the polymers are more expensive on a price-per-weight basis, overall operating cost is lower because of reduced dosage. The second is that there is no need of tight control of pH around the isoelectric

point since bridging can occur independent of pH. The third benefit is that there is reduced sludge disposal and reduced disposal costs. In addition, polyelectrolytes used as coagulation aids have been found to enhance the settling speed³⁰. Theoretical

aspects of such polyelectrolyte bridging have also been reviewed³¹.

Several polymers can be used as flocculants. Some popular examples are polyDADMAC, polyethylamine, polyacrylamides, polyvinylamine, polyethylene oxide, and polystyrene derivatives³²⁻³⁵. Furthermore, several biopolymers such as tannin³², laccases³⁶, chitosan^{37, 28} and others³⁸ have been proposed as bioflocculants. The advantages of bioflocculants are biodegradability and nontoxicity. Other sources of polymeric coagulants have also been explored. Yin³⁹ reviewed the plant-based sources of coagulants while Sulkowski et al⁴⁰ described a technique by which polystyrene wastes can be converted to water soluble polymeric flocculants.

Since flocculation is such an important industrial process a lot of effort has been expended on the modeling, design and optimization of the process. A number of research works^{26, 16, 41-42} have proposed the use of population balance modeling to model the flocculation process. Chen et al⁴³ discuss the rational design of polymers for use as flocculants. Attempts were also made to optimize flocculation conditions for industrial use⁴⁴.

Some other applications of flocculation have been also studied in the literature. The use of modified chitosan in breaking of o/w emulsions was studied³⁷. The increased uptake of ⁹⁰Sr and ¹³⁷Cs from nuclear process waste by using polyacrylamide as flocculant was discussed⁴⁵. Further, extracellular bioflocculants (EBFs) have been used for removal of cells and cell debris from culture broths³⁸. The bridging of nanoparticles was demonstrated⁴⁶ and found that a single adsorbing chain can collect multiple particles in a stable multiplet.

Detergency

Polymers have several roles to play in the process of washing. Most of these involve the adsorption of polymers onto the soiled cloth surface. For instance, amphiphilic polymers can be used to release and disperse soil contamination in the cloth via the roll-up and solubilization mechanism⁴⁷.

Biopolymers such as proteases and especially subtilisin⁴⁸ and lipases such as Lipolase®, a commercial soluble preparation supplied by Novozymes⁴⁹ are used to break down proteins and fats adhering to the cloth surface. These enzymes accomplish this by adsorption onto cloth. A recent review⁵⁰ has highlighted that these enzymes allow use of lower wash temperatures and thus reduce environmental load. The review also mentioned the use of these enzymes in leather and contact lens cleaning, clearing of clogged drains, toilet bowl cleaning. The other applications are the removal of dirt/ cattle manure from animals.

Another interesting work⁵¹ deals with the use of proteases and lipases in removing strongly adsorbed proteins and lipids from ultrafiltration (UF) membranes used in abattoir effluent treatment. The major limitations of enzyme usage are the low stability of enzymes in their native state and their prohibitive cost⁴⁹.

Polymers are also included in detergent formulations as anti-redeposition agents. These polymers attach themselves via physisorption on the cloth surface and prevent the redeposition of the soil back onto the cloth. Carboxymethylcellulose⁷ and lipases⁴⁹⁻⁵⁰ find popular use as anti-redeposition agents.

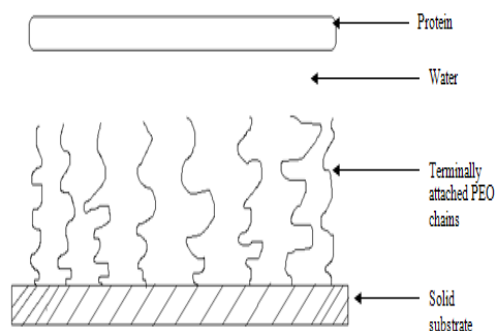
Biomedical Applications

Polymers have been used as biomaterials in the area of biomedical engineering for quite some time. One of the most important polymers used in biomedical engineering is polyethylene glycol (PEG). This polymer is highly biocompatible and is used as biocompatibilizer in many applications. Indeed so immense is its popularity that a new word "pegylation" has been coined to describe the attachment of PEG to a surface. PEG has its application in biocompatibilizing biomaterials and in manufacture of "Stealth Liposomes". These are elaborated below.

Biomedical materials

When a biomedical material is implanted into a living tissue, a cascade of host reactions occur at the interface between the tissue and the material, known as inflammatory response. This inflammatory response can lead to thrombosis and embolism⁵³. A key step in this response is the adsorption of proteins at the surface of the biomaterial. An important goal regarding the design of biocompatible materials is to create surfaces that minimize interaction of proteins⁵². By minimizing protein adsorption, it is possible to prevent the rejection of the implant by the body. Biomaterials on which end-tethered polymer brushes of PEG are formed have been used to this end (Fig 6).

Fig 6: Schematic diagram showing a PEG brush (A collection of end-tethered PEG chains) repelling the advance of a protein molecule



Stealth liposomes

Another challenge in biomedical engineering is controlled drug delivery. Medical drugs have a specific therapeutic range of concentration within which they are effective. Below this range, they are ineffective in the treatment of infection and disease and they can be toxic to healthy cells at higher concentrations. Obviously, it is desirable to maintain a constant level of drug concentration within the therapeutic range for an extended period of time.

One way is to encapsulate drugs in liposomes⁵⁴. A liposome is a vesicle made of lipids arranged as a bilayer. Liposomes have a hollow compartment that can be filled with the relevant drug. These liposomes can fuse with the cell membrane (which is also a lipid bilayer), thus delivering the liposome contents. On the other hand, liposomes can also allow constant diffusion of drug into the bloodstream at a uniform rate.

One major hurdle in this technique is that the liposomes are absorbed into the reticuloendothelial system (RES) after circulating for sometime in the blood stream. To increase the potency of the drug-carrying liposomes, a longer circulatory life is desirable. This can be accomplished by pegylating (i.e. attaching PEG chains to) the liposomes. The attached PEG, being highly biocompatible, masks and thereby prevents detection of the liposomes by cells of the RES⁵⁵. This allows the liposomes to circulate longer in the blood. Such pegylated liposomes are called "stealth liposomes" and are highly promising for controlled drug release⁵⁶.

In addition to stealth liposomes, another technique has been proposed for forming hollow carriers that hinges on polymer adsorption. Antipov and Sukhorukov⁵⁷, Johnston et al⁵⁸ and Gil et al⁵⁹ reviewed a novel type of polymer micro- and nano-capsules whose shells are fabricated by adsorption of polyelectrolytes onto the surface of colloidal particles which act as templates. The shell thickness and permeability can be readily fine-tuned and hence these capsules are especially suitable for controlled drug delivery.

Conclusions

In the above study the authors reviewed some of the preeminent applications of polymers at interfaces. New applications are still emerging. The revolution created by molecular biology and nanotechnology can usher in innovative technologies based on the interfacial behaviour of polymers. This article will be very helpful for molecular biology and for those engineers working in the field of polymers. It is the requirement of the present time to explore various polymers at molecular level as they are a helpful tool for the techniques of modern science and technology.

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