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Surface Engineering of Polymer Membranes

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Preface

Surface Engineering of Polymer Membranes embraces those processes which modify membrane surfaces to improve their in-service performance. It means 'modifying the surface' of a membrane to confer surface properties which are different from its bulk properties. The purpose may be to minimize fouling, modulate hydrophilicity/hydrophobicity, enhance biocompatibility, act as a diffusion barrier, provide bio- or chemical functionalities, mimic a biomembrane, fabricate nanostructures or simply improve the aesthetic appearance of the membrane surface. The book begins with the basics of the surface engineering of polymer membranes, including surface modification, biomimicking, enzyme immobilization, molecular imprinting and the various methods of the spectroscopic and structural study of membrane surfaces. These are followed by descriptive treatments of topics such as surface modification by graft polymerization and macromolecule immobilization, the construction of biomimetic surfaces and their functionalities, enzyme immobilization and bioactivity, molecular recognition and nanostructured surfaces. This book provides a unique synthesis of our knowledge of the role of surface chemistry and physics in membrane science and technology. I sincerely hope and anticipate that this book, which contains plentiful information on the many and varied aspects of membrane surfaces, will be useful to anyone interested or involved in this fascinating and technologically important research area.

Since 2001 I have been devoted to the study of surface modification and enzyme immobilization on polymeric membranes. It is unimaginable that the work could have been carried out, year-by-year, without financial support. Therefore I gratefully acknowledge the National Natural Science Foundation of China (Grant nos. 20074033, 50273032, 20474054 and 20774080), the National Natural Science Foundation of China for Distinguished Young Scholar (Grant nos. 50625309), the High-Tech Research and Development Program of China (Grant no. 2002AA601230 and 2007AA10Z301), and the Zhejiang Provincial Natural Science Foundation of China (Grant no. Z406260) for the financial support.

It is indeed a great pleasure to extend my "thank you" to all my colleagues and students for their dedication to our research projects. Especially, Chapter 3 profits from the work of Bei-Bei Ke, Chapter 4 is part of the thesis by Meng-Xin Hu, Chapters 5 and 7 are based on the parts of theses by Qian Yang and Zheng-Wei Dai respectively, Chapter 8 profits from the work by Ai-Fu Che and Yun-Feng Yang, and Chapters 9 and 10 are benefit from the thesis by Zhen-Gang Wang. Their efforts are deeply appreciated and acknowledged. Finally, I would like to thank the editorial staff of Springer Verlag and Zhejiang University Press for their assistance.

Zhi-Kang Xu
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Surface Engineering of Polymer Membranes: An Introduction

Polymeric separation membranes develop rapidly and have been applied in many fields. Filtration with polymer membranes covers the separation of industrial chemicals, purification of laboratory products and treatment of drinking water. For all these processes, the performance limits are clearly determined by the membrane itself. Flux and rejection of a membrane process such as microfiltration or ultrafiltration are mainly influenced by size exclusion. Nevertheless, surface properties of the membrane also play a crucial role. It is because membrane fouling, induced by adsorption of matter onto the membrane surface or deposition into the pores, is mainly controlled by the surface properties. For example, a hydrophobic membrane surface is apt to cause adsorption of protein or other solutes due to hydrophobic interactions. As is well known, membrane fouling will decline the flux and deteriorate the selectivity. Meanwhile, the products must meet the ever stricter environmental or safety standards. A membrane separation system should consist of a membrane with stable and reliable performance. Therefore, the first objective of polymer membrane surface engineering is to enhance the surface properties of the membrane by modulating its surface chemistry and physics, and hence improve the performance of the membrane.

Another important objective is to achieve surface functionalization for polymer membranes. It is well known that the membrane process has been used in many applications. Some of them are relatively mature, while others are still in the course of development. The developing technologies, including those for biocatalysis and sensing, generally require a functional membrane surface. What is more, their performances mainly depend on the functionality of the membrane surface. For instance, a functional surface immobilized with enzyme can be applied in an enzyme-membrane bioreactor as well as in biosensors, in which the activity retention and stability of the immobilized enzyme are essential. It is accepted that characteristics of the membrane surface can remarkably affect the enzyme activity and stability. Therefore, based on the strategies for surface modification, a functional membrane surface can also be constructed. This objective is exciting because it means that the areas of application for polymer membranes can be greatly extended.

To achieve the two above-mentioned objectives, it is easy and effective to use surface modification in the surface engineering of polymer membranes. "Grafting from" and "grafting to" are two commonly used strategies. The "grafting from" method utilizes active species existing on a membrane surface to initiate the polymerization of monomers from the surface. Usually this strategy is accomplished by treating a substrate with plasma and glow-discharge to generate immobilized initiators, followed by polymerization. On the other hand, for the "grafting to" method, polymer chains carrying reactive anchor groups at the end or on the side chains are covalently coupled to the membrane surface, which is also referred to as macromolecules immobilization in this book. Chapters 4 and 5 mainly focus on these two methods, respectively. In these two chapters, surface modifications of polymer membranes are comprehensively summarized, which include chemical graft polymerization, plasma or glow-discharge induced graft polymerization, UV-induced graft polymerization, high energy radiation-initiated graft polymerization, and immobilization of synthetic polymers and biomacromolecules. Applications of these surface modified membranes are also discussed from various aspects.

As inspired by the cell membrane, biomimetic modification is also introduced to realize membrane surfaces with the desired surface properties or functions. According to the fluid mosaic model proposed by Singer and Nicholson, the cell membrane is composed of a semipermeable lipid bilayer, which consists of three classes of amphipathic lipids, i.e. phospholipids, glycolipids and steroids. The relative composition of each depends upon the type of cell, but in the majority of cases phospholipids are the most abundant. Thus, the construction of membrane surfaces with phospholipid moieties is discussed in Chapter 6. In this chapter many kinds of membrane surfaces with phospholipid moieties are present. It is not hard to see that the modified membranes are highly biofouling resistant because they possess considerably biocompatible surfaces. This type of membrane can also suppress non-specific adsorption of proteins or cells, which is also beneficial to its biomedical applications.

Differing from phospholipid, carbohydrates have often been found on the surface of nearly every cell membrane in the form of polysaccharides, glycoproteins, glycolipids or/and other glycoconjugates. The carbohydrates on the external cell membrane, known as the glycocalyx, play essential roles in many biological functions which can be classified in two opposing ways. One serves as sites for the docking of other cells, biomolecules and pathogens in a more or less specific recognition process. The other contributes to steric repulsion that prevents the undesirable non-specific adhesion of other proteins and cells. Both these two functions rely on the carbohydrate-protein interactions. Advances in membrane surface glycosylation constitute Chapter 7 in which modification with natural polysaccharides, such as heparin and chitosan, as well as synthetic glycopolymers is described. The surface glycosylation provides the membrane with a surface of high hydrophilicity and biocompatibility. Furthermore, the specific recognition between the carbohydrates and proteins endows the membranes with some interesting functions, which may be useful in protein isolation/purification.

A molecular imprinting technique is also a way of creating a membrane surface with a specific recognition function, which forms Chapter 8. Compared with a glycosylated surface, a molecular imprinted surface is even more flexible. As we know, molecular recognition involves selection and recognition according to the shape, size and the interaction characterized with selectivity between a ligand and a given receptor. A molecular imprinting technique just originates from molecular recognition, which can also achieve recognition at the molecular level. A molecular imprinted membrane can be used to separate template molecules from others of similar molecular size, or to concentrate template molecules. This extends the size exclusion mechanism for a separation membrane by introducing specific recognition. For example, such membranes can separate amino acid from its enantiomers though the molecular size is the same. Moreover, a molecular imprinted membrane can act as a recognition element for sensor design. In Chapter 8, the basic theory of the molecular imprinting technique, methods for molecular imprinted membrane preparation (including surface imprinting method), the separation mechanism of the molecular imprinted membranes and their applications are summarized.

A membrane with a biocatalytic surface is another important example of surface functionalization, which is the topic of Chapter 9. The enzyme is a kind of catalyst that is not only efficient and safe but also environmentally benign and resource and energy saving. Using a membrane as the support for enzyme immobilization can simultaneously realize the functions of catalysis and separation. However, there are many factors affecting the performance of an immobilized enzyme, such as surface chemistry, membrane structure, immobilization procedure as well as enzyme characteristics, enzyme loading and reaction condition. In this chapter, immobilization of an enzyme on polymer membranes is thoroughly reviewed. Various procedures for the immobilization of different kinds of enzymes on a great variety of membrane materials, including natural and synthetic materials, are present here. In addition, the applications of membranes with a biocatalytic function in bioreactors and biosensors are also summarized.

In the past decade, nanofibrous membranes prepared via an electrospinning technique have received considerable interest because of their large surface area to volume ratio and high porosity. Most importantly, an electrospinning technique is versatile and shows a good prospect for the fabrication of nanofibrous membranes on a large scale. When compared with traditional filter media such as a phase inversion membrane or fibrous membrane at the micron scale, an electrospun nanofibrous membrane used for filtration may have an extremely high efficiency. It should be attributed to the nano-sized fibers. Thus, this topic is sufficiently important to warrant its own treatment in Chapter 10. In this chapter, we focus on the functionalization of nanofibrous membranes, and those with a biocatalytic function and affinity function are particularly emphasized.

Before the specific description of the modification and functionalization of polymer membrane surfaces, some general methods for surface modification and characterization, which are closely related to polymer membranes, are introduced in the following chapters. Characterizing the modified surface is not only important to understand the relationship between the membrane surface structure and its properties but also important to provide guidance for surface modification. It is well known that membrane surface properties are affected by many factors such as the chemical composition, morphologies and structures, wettability, and biocompatibility. Therefore, in Chapter 2 membrane surface characterization is introduced from the above-mentioned aspects. The following characterization techniques are briefly introduced: attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), energy dispersive X-ray spectroscopy (EDS), optical microscopy, laser confocal scanning microscopy (LCSM), scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM), atomic force microscopy (AFM), contact angle measurement, and some evaluation methods for the biocompatibility of membrane surfaces. On the other hand, methods for the functionalization of the polymer membrane are summarized in Chapter 3 from the aspects of surface modification, molecular imprinting, and enzyme immobilization. For surface modification in particular, several methods are presented, which include coating, self-assembly, chemical treatment, plasma treatment, and graft polymerization.

Overall, membrane science and technology is still in a period of enormous progress and development. The steady rise to 3.442 in 2006 of the impact factor of the *Journal of Membrane Science*, the top journal in this field, is excellent proof. In our view, surface engineering is one of the most important fields in all of membrane science. In this book, an attempt has been made to cover the most important trends in the area of surface modification and functionalization of polymer membranes. However, due to the wide diversity of the field, selections have to be made which also reflect the particular interests of the authors.

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Techniques for Membrane Surface Characterization

In recent years, the surface engineering of polymer membranes through surface modification and surface functionalization has received significant attention. Since the properties of a membrane surface are very important for practical applications, it is important to have the means to characterize and measure those structures and properties. In fact, surface characterization is not only important for understanding the relationship between the membrane structure and its properties but also for guiding surface modification. It is well known that various aspects of a membrane surface, which include chemical composition, morphology and topography, wettability, and biocompatibility, can affect the properties and applications remarkably. Many kinds of surface characterization techniques may be applied to study the surface properties of polymer membranes. In this chapter, techniques for the characterization of a polymer membrane surface are reviewed, which include attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), energy dispersive X-ray spectroscopy (EDS), optical microscopy, laser confocal scanning microscopy (LCSM), scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM), atomic force microscopy (AFM), contact angle measurement, and some evaluation methods for the biocompatibility of membrane surfaces.

2.1 General Principles

2.1.1 Sample Preparation

A number of general ideas can be applied to all polymeric surfaces. Of course, a polymeric membrane surface is not the exception. Sample preparation is of great importance for every characterization method, which determines the reliability of the obtained results. Bad sample preparation gives rise to artifacts.

Needless to say, a sample for characterization should reflect, as closely as possible, the membrane being subjected to the separation process, whether it be the chemical composition or the physical morphologies. Therefore, first of all, contamination on the membrane surface should definitely be avoided. Every step in the analysis procedure must be carefully performed. Contamination is easily introduced from the environment such as from the atmosphere and even from the packaging bag. On the other hand, some residual matter may also act as a contaminant, especially for the membrane after modification. For example, the subjected membrane grafting polymerization process should be thoroughly rinsed or cleaned to remove the residual un-reacted monomers or the embedded un-grafted polymer. Secondly, unlike other smooth polymer film surfaces, a polymer membrane is porous and hence preserving the original look of the porous membrane is a matter of special importance in most cases. For some characterization methods, a vacuum is required and then drying is necessary for sample observation. Consequently, problems can arise if a wet membrane specimen is dried under intense conditions because the membrane porous structure may be damaged or altered by the capillary forces (Mulder, 1996). Various methods can be employed to prevent this. For example, as water has a high surface tension, a sequence of non-solvents for the membrane such as water, ethanol and hexane can be used one by one to reduce the capillary forces during drying. In this sequence, the surface tension of the non-solvent decreases gradually and the last hexane has a very low surface tension and can be easily removed.

2.1.2 Where is the Surface?

It is well known that the surface property is very important. However, what is meant by a membrane surface? Where is the surface? Ideally the surface should be defined as the plane at which the membrane terminates, in other words, the last atom layer before the adjacent phase begins (Bubert and Jenett, 2002). Unfortunately such a definition is impractical because the effect of termination extends into the solid beyond the outermost atom layer, especially for a membrane which is porous and rough. Furthermore, the "surface" is sometimes a changeable concept for different methods of analysis, because different methods provide varying degrees of information at different depth profiles. For example, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is a most widely used surface characterization technique and supplies the characteristic absorption bands of functional groups with a depth of 0.1~10 μm. But another technique, X-ray photoelectron spectroscopy (XPS), is more surface-sensitive, which provides the amount and state of elements presented in the surface layer with a depth of about 10 nm. In addition, it is worth noting that the analysis depth may be different or changeable even for a certain kind of characterization technique, which is very useful in analyzing a chemically gradient surface. As we know, the analysis depth for XPS changes with the take-off angle while that of ATR-FTIR varies a lot with the wavelength, incident angle, etc. In conclusion, it is extremely important to choose a suitable technique for the surface characterization. The analysis depth profiles of some typical techniques are shown in Fig.2.1.

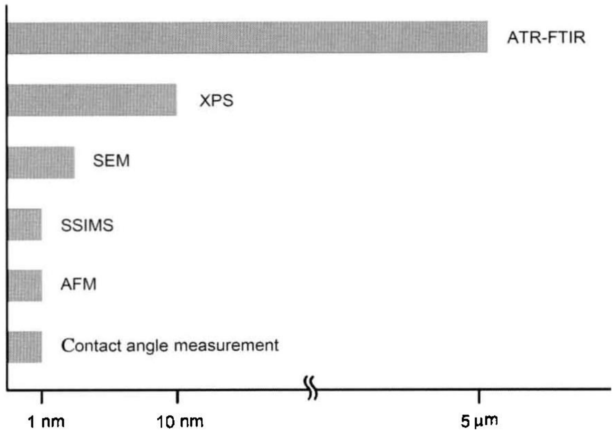

Fig. 2.1. Estimated analysis depth profiles of some characterization techniques

2.1.3 Is it Really the Surface?

If you want to observe a polymer surface (a polymer membrane surface is of course included), it does not seem to be such a very easy matter. Maybe the surface works like magic. That is because solid polymers have non-equilibrium structures with chains rotating and repeating and exhibit a range of relaxations and transitions in response to time, temperature and other environmental changes. Surface reconstruction of polymers has been reported extensively from both theoretical and experimental points of view (Chen and McCarthy, 1999). In general, reconstruction tends to concentrate at the surface of the component that is the most similar to the phase above it. As we know, some membrane processes, such as wastewater treatment, ultrapure water production, hemodialysis and seawater desalinization, are performed in an aqueous environment. Meanwhile, in most cases, additives are used for membrane preparation to modulate the structure or enhance the performance. These additives, including some kinds of water-soluble polymers, are often highly hydrophilic. They will be enriched at the membrane surface in an aqueous environment. However, under vacuum or in the atmosphere they may bury into the membrane bulk and be replaced by other components with a low surface energy. As a result, the possible changes induced by the environments should be considered before the analysis of a membrane surface. The reconstruction of a polymer surface is illustrated in Fig.2.2.

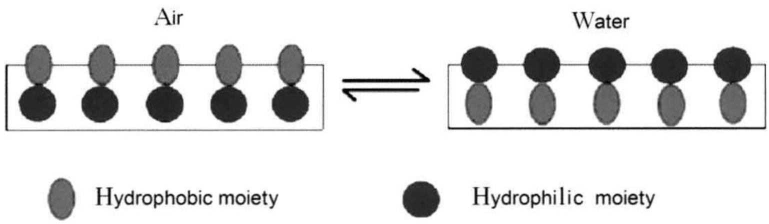

Fig. 2.2. Illustrated reconstruction of polymers under different environments

2.1.4 Invasive or Non-invasive

Although a membrane surface is at the forefront of interacting with its surroundings and the surface influences many crucially important properties of the membrane, up to now observation of the surface in a simple, direct, *in situ* and high-resolution way, presenting a real world of atoms or molecules at the outermost surface layer, is still challenging. Mainly because reconstruction of a membrane surface can take place, techniques that provide *in situ* real-time monitoring of the membrane surface during membrane processes are attractive. Methods requiring a high vacuum, such as scanning electron microscopy (SEM), are generally invasive while most optical techniques are non-invasive (Chen et al., 2004). These non-invasive techniques can be used to monitor the changes of the surface state, such as the adsorption of protein or the formation of membrane fouling. Unfortunately, the optical techniques are mostly of low resolution and other special conditions such as transparent membranes are required. Phase contrast X-ray micro-imaging with synchrotron radiation has been shown to be a powerful tool for non-invasive observation of phenomena occurring in membrane filtration processes (Yeo et al., 2005). This technique is able to observe the deposition of particles inside the lumen of a hollow fiber membrane and also detect deposition and fouling within the membrane structure. This means that the inside surface of a membrane may be observed *in situ*. Besides, the resolution of this technique is of the order of 1 μm, which is superior to other available non-invasive techniques. More and more techniques are becoming available for *in situ* real-time observation. Therefore, the real world and original appearance of the membrane surface will be progressively approached.

2.2 Chemical Composition of Membrane Surfaces

In most cases, analysis of the chemical composition of the membrane surface is necessary. For example, we want to know the chemical changes of the surface before and after surface modification. We also want to know what kind of foulants is adhered to the membrane surface. As a result, the following important questions should at least be answered: