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Research Article

FABRICATION OF NANO-STRUCTURED SURFACES BY FINE TUNING OF DEPOSITION PARAMETERS IN CHITOSAN/PSS POLYELECTROLYTE MULTILAYERS

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ABSTRACT

The fabrication of chitosan/polystyrene sulfonate (CHI)/(PSS) polyelectrolyte multilayer on different polymeric supports (polyether sulfone, polycarbonate and nylon), is discussed in the present work. The permeation of model protein BSA through these multilayer membranes was carried out under ultrafiltration conditions. Different multilayer systems were prepared by varying the parameters such as nature of the polymeric support, pH and molecular weight of polyelectrolyte. Build up of multilayers on polymeric support was monitored by measuring area under the sulfonate peak at 1033 cm^{-1} in the FTIR spectrum. No appreciable rejection of BSA was observed when CHI/PSS multilayers were fabricated on polycarbonate and nylon supports even after 15 bilayer coating. When multilayers were fabricated on polyether sulfone membranes, more than 90% rejection of BSA was observed with 5 bilayer coated membrane. This study reveals that pH and molecular weight of the polyelectrolyte has decisive role in the multilayer build up.

Keywords: Polyelectrolytes, Polyelectrolyte Multilayers, Layer-by-layer assembly, Nanostructured films.

1. INTRODUCTION

Polyelectrolytes are macromolecular species which dissociate into highly charged polymeric molecules in water or other ionizing solvents. These macromolecules carry covalently bound charged groups, (cationic or anionic) and low molecular counterions. Polyelectrolytes which bear both cationic and anionic repeat groups are called polyampholytes, example includes polypeptides and DNA. Both natural and synthetic polyelectrolytes are used in a variety of industries.

Polyelectrolytes can be divided into weak and strong types. A strong polyelectrolyte is one which dissociates completely in solution for most reasonable pH values. Weak polyelectrolytes are not fully charged in solution, and moreover their fractional charge can be modified by changing the solution pH, counterion concentration, or ionic strength. Currently a lot of research is going on for the development of biocompatible polyelectrolytes for implant coating, controlled release and other applications [1-5].

Nanostructured films or nanoscopically organized films are of great scientific interest due to their potential applications including design of molecular architectures and novel functionalities, sensing, microelectronics, photonics, material separation, controlled drug delivery, molecular recognition etc. Ultrathin films of controlled thickness can be prepared by the recently developed layer-by-layer (LBL) method which involves deposition of cationic and anionic polyelectrolytes alternately on polymeric supports. By varying factors like pH, ionic strength, number of bilayers, nature of polyelectrolyte etc. it is possible to fine tune the permeation and selectivity of PEM membranes.

1.1. Layer-by-layer assembly (LBL) of polyelectrolytes

The layer-by-layer (LBL) assembly technique involves alternate dipping of a substrate or a solid support in two oppositely charged polyelectrolytes along with water rinse steps in between to remove any extra material that is loosely bound to the surface. Thus, one can build as many layers as needed depending on the particular type or requirements of the experiment. Ultrathin films could be built offering high flux and selectivity for membrane separations, filtrations and purification applications. Thicker membranes could also be built offering hydrophobic coatings, hydrophilic coatings or anti-corrosive coatings. Multilayers reported in the literature had thickness that ranged between 10 nm and 10 μm [6].

The process of multilayer formation is based on the attraction of opposite charges, and thus requires a minimum of two oppositely charged molecules. Consequently, one is able to incorporate more than two molecules into the multilayer, simply by immersing the substrate in as many solutions of polyelectrolytes as desired, as long as the charge is reversed from layer to layer. In addition, individual nanoparticles may be incorporated into any or all of the monolayers, allowing wide design opportunities for thin films with specific or multifunctional properties [7].

Polyelectrolyte complexation is the driving force for multilayer formation. However, depending on the chemical nature of the polyions employed for deposition, electrostatic contribution should vary and other interactions such as van der Waals, hydrogen bonding or charge transfer may also be involved.

1.2. Advantage of LBL assembly technique

The LBL assembly technique was first mentioned by Iler in 1966 [8]. In 1991, however, Decher and Hong expanded this technique and brought it to the forefront of materials science and engineering [9]. The LBL technique is superior, in many respects, to other deposition techniques that are reported in the literature such as vacuum deposition, solvent casting, spin coating or Langmuir-Blodgett (LB) deposition. Vacuum deposition requires specialized expensive instrumentation and specific types of substrates. Solvent casting produces thick and non-uniform films. The earliest technique used to fabricate multilayer films was invented by Langmuir and Blodgett to make LB films. LB films are highly ordered and have uniform-controlled thickness. However, they have several limitations. The requirements for substrates are stringent: they must be smooth, homogeneous and have regular shape. Furthermore, LB fabrication requires expensive equipment. LB multilayers have limited stability against solvents and thermal treatments. Also, it is a slow technique. [10-12]. On the other hand, the LBL technique is a very robust, reproducible, durable, cost effective and environmental friendly method. It is done at room temperature, so there is no need for any vacuum equipment or special instrumentation. It can be used to assemble various types of materials, polymers, composites, clay, proteins, dyes, carbon nanotubes or nanoparticles [13-16]. Also, it can be coated on various kinds of substrates such as silicon, gold, platinum, plastics, glass, quartz, stainless steel clay, nanoparticles, blood cells and colloidal particles. The whole process can be automated making the coating procedure less time consuming and applicable for commercial purposes where productivity and labour are major problems. Above all, this technique offers very precise control over thickness and unprecedented uniformity of the coating down to the subnanometer scale.

The LBL procedure can be applied for the fabrication of multicomposite films ie, nanoscopic assembly of hundreds of different materials in a single device using environmentally friendly, low- cost techniques. The materials can be small organic molecules, inorganic compounds, macromolecules, biomacromolecules such as proteins or DNA, or even colloids (metallic or latex particles) [17-19]. The technique can be applied to solvent accessible surfaces of almost any kind and any shape; the more interesting ones are microcapsules, colloids or biological cells.

1.3. Polyelectrolyte multilayer films for membrane applications

The exceptional thinness of polyelectrolyte multilayer membranes (PEM) provides high flux for selective separations. PEMs are better suited for surface modification, where uniformity is at a premium and a minimal thickness of mechanically film is advantageous. Since 2000, a significant number of studies have been reported using the layer-by-layer assembly technique of polyelectrolytes to assemble thin film coatings for membrane separations [20-29]. Most works are concerned with separation of ions, gases and small neutral molecules under nanofiltration conditions. Several factors such as pH, ionic strength, number of bilayers, nature of polyelectrolyte etc. have been shown to affect the permeability and the selectivity of the assembled membranes. By varying these factors it is possible to fine tune the permeation and selectivity of multilayer membranes. Polyelectrolytes with low charge density are capable of forming less cross-linked multilayers, which in turn result in swollen membranes that are capable of separating larger molecules like proteins.

The fabrication of chitosan/polystyrene sulfonate (CHI)/(PSS) polyelectrolyte multilayer on different polymeric supports is discussed in the present work. Different multilayer systems were prepared by varying the parameters such as nature of the polymeric support, pH and molecular weight of polyelectrolyte solutions.

2. MATERIAL AND METHODS

Chitosan (CHI, medium MW, and high MW, 75-85% deacetylated) and Poly styrene sulfonate (PSS, MW 70,000, 30 wt % in water) were purchased from Sigma Aldrich and were used as polycations and polyanions respectively. BSA (MW 67,000) was purchased from SRL, Mumbai. Polycarbonate, nylon and Supor®- 450 (Polyether sulfone) microfiltration membranes of 0.45 μm pore diameter from PALL life science was used as support membrane for LbL assembly. Ultrapure water (18.2 MΩ.cm) obtained from Cascada AN™ water purifying system (Pall Corporation) was used for all experiments.

2.1. Fabrication of multilayers

Multilayers were coated alternately from 0.01 M solutions of CHI and PSS solutions having pH 1.7 and 2.1. The support membranes were kept in water overnight before multilayer preparation. The pH of the polyelectrolyte solutions was adjusted with 1 M HCl. The support membrane was dipped in CHI and PSS alternatively for 15 minutes with washing in water in between. The pH of the polyelectrolyte solutions were adjusted to 1.7 by HCl. Bare membrane was first dipped in 0.01M chitosan solution in water (molarities of polyelectrolytes were taken with respect to repeating unit), at pH 1.7. The dipping time was 15 minutes (step 1). After dipping, the membrane was rinsed with 50 ml distilled water for 1 minute (step 2). Then the membrane was dipped in 0.01 M PSS in water at pH 1.7 or 0.01 M PSS in 0.1 M NaCl at pH 1.7 for 15 minutes (step 3). The membrane was then rinsed with 50 ml distilled water (step 4). Thus, one CHI/PSS bilayer (bl) is formed on the supporting membrane by performing steps 1-4 (fig.1). The dipping process was repeated till required number of bilayers was formed. The thickness, porosity and other characteristics of the multilayers strongly depends on the dipping conditions. So in order to get reproducible results care is taken to prepare multilayers under the same conditions of pH, concentration, dipping time, rinsing time etc.

2.2. Ultrafiltration

Ultrafiltration experiments were performed with amicon 8050-ultrafiltration cell (Millipore). All ultrafiltrations were carried out at 5-10 psi pressure at 400 rotations/minute (rpm) at room temperature (28-30ºC). The multilayer coated membrane was fixed at the bottom of the cell. A definite volume of the solution to be filtered is taken in the cell, the lid is closed and the cell is pressurized by nitrogen gas.

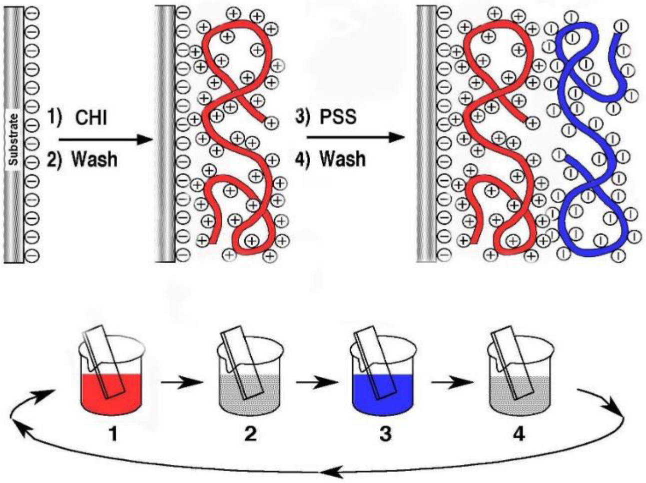


Fig. 1: Scheme of layer-by-layer adsorption of polyelectrolytes on porous supporting membrane. Multiple repetition of steps 1&2 and 3&4 leads to the ultrathin separating layer

2.3. UV-visible spectroscopy

Concentration of BSA in permeate was determined spectrophotometrically at 280 nm with a Shimadzu UV-visible spectrophotometer (UV-1700 Pharmaspec).

2.4. Fourier Transform Infra-Red spectroscopy (FT-IR)

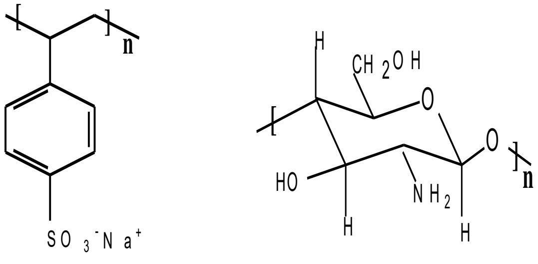
Build up of Chitosan /PSS multilayers on polyether sulfone membranes were characterized by Shimadzu 8400S spectrometer.

3. RESULTS AND DISCUSSION

3.1. Film characterization

Chitosan-Polystyrene sulfonate is selected as the polyelectrolyte pair. The structures of the polyelectrolytes are shown in fig.2. Chitosan is the deacetylated derivative of chitin, which is the second most abundant polysaccharide found on earth next to cellulose.

Chitosan has a great potential for a wide range of uses due to its biodegradability, biocompatibility, anti-microbial activity, non-toxicity, and versatile chemical and physical properties.



PSS **Chitosan**

Fig. 2: Polyelectrolytes used for coating

Careful selection of polyelectrolyte pair as well as polymeric support is important in conducting permeation studies using polyelectrolyte multilayer membranes. Polymeric supports selected for fabrication of CHI/PSS multilayer coating in the present study were polycarbonate, nylon, and polyether sulfone (supor) membranes. Multilayers were fabricated on polycarbonate, nylon and polyether sulfone membranes and permeation of model protein BSA under ultrafiltration conditions was carried out at selected pH 9 (above isoelectric point), at pH 4.8 (isoelectric point) and pH 3.5 (below isoelectric point). No appreciable rejection of BSA was observed when CHI/PSS multilayers were fabricated on polycarbonate membranes even up to 15 bilayers at all the selected pHs. Even after 15 bilayers of CHI/PSS coating on nylon support, only 25% rejection of BSA was observed at pH 9. A better rejection (95%) of BSA was observed at pH 9 with 7 bilayers when CHI/PSS multilayers were fabricated on polyether sulfone (supor) membranes [20]. So for further permeation studies of proteins, CHI/PSS multilayers were fabricated on supor membranes.

Table 1: Percentage rejection of BSA with number of CHI/PSS bilayers fabricated on different polymer supports

Number of CHI/PSS bilayers	% Rejection of BSA at pH 9		
	Polycarbonate	Nylon	Polyether sulfone
0	0.15	0.29	0.90
5	2.60	5.35	58.5
10	4.86	7.94	94.7
15	5.85	25.86	91

The formation of multilayers on the surface of bare supor membrane has been examined using Scanning Electron Microscopy (SEM). Fig. 3 shows SEM images of polyether sulfone support and a 7 bilayer CHI/PSS on supor membrane. The presence of polyelectrolyte multilayer is clearly seen in the image.

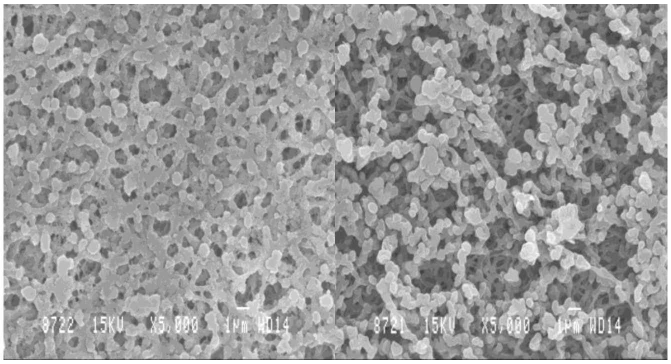


Fig. 3a **Fig. 3b**

Fig. 3: SEM pictures of bare supor membrane (3a) and 7 bl CHI/PSS coated membrane (3b) [20]

3.2. Effect of coating pH

The thickness and porosity of polyelectrolyte multilayers depends on a number of factors such as pH and charge density of the polyelectrolyte solution. CHI/PSS multilayers on polyether sulfone support were prepared from chitosan and PSS solutions having pH 1.7 and 2.1. The multilayer build up was followed by measuring the area under the sulfonate peak in the FT IR spectrum. The area under the plot of the sulfonate peak at 1033 cm^{-1} is larger for the one at pH 1.7. As the thickness of the film is directly proportional to the amount of polyelectrolyte adsorbed, it is assumed that the PEM formed at pH 1.7 is slightly thicker compared to the PEM formed at pH 2.1.

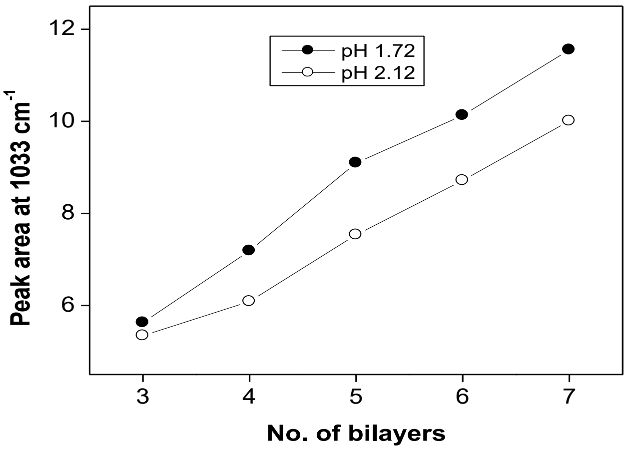


Fig. 4: Area under the sulfonate peak (1033 cm^{-1}) in the FT-IR spectrum as a function of the number of deposited layers at two different pHs 1.72 and 2.12

By varying the pH of the polyelectrolyte solution, the extent of ionization and hence the degree of multilayer cross-links can be varied. This can affect the permeability and flux of the multilayer membrane. PSS will be more ionized at pH 2.1. Cross-linking may be more and the resulting films are consequently thinner. The pH dependent variation of thickness of PEM coating was also reported by Salloum *et al.* [21]. They observed that the thickness of PAA/PAH multilayer vary from 5-80A° with small variation in pH of the polyelectrolyte solutions. In addition, control over the bulk and surface composition of the resultant multilayer thin films is readily achieved by simple pH adjustments.

3.3. Effect of molecular weight of polyelectrolyte

Another parameter that may affect the efficiency of multilayer coating is the molecular weight of the polyelectrolytes. Early reports indicate that molecular weight of the polyelectrolyte has some influence, even though, not stronger as compared to pH and ionic strength [22-24]. CHI/PSS multilayer assembly was prepared on polyether support by using two chitosan samples of different molecular weights (chitosan, medium MW and chitosan, high MW). Two sets of multilayer assemblies, *viz*. CHI (medium MW)/PSS at pH 1.7 and CHI (high MW)/PSS at pH 1.7, with varying number of bilayers were prepared. The coating efficiency was followed from the FT- IR data. In both cases, the sulfonate peak at 1033 cm^{-1} was found to increase with increasing number of bilayers. It was observed that the coating was more effective with CHI (medium MW)/PSS multilayer assembly.

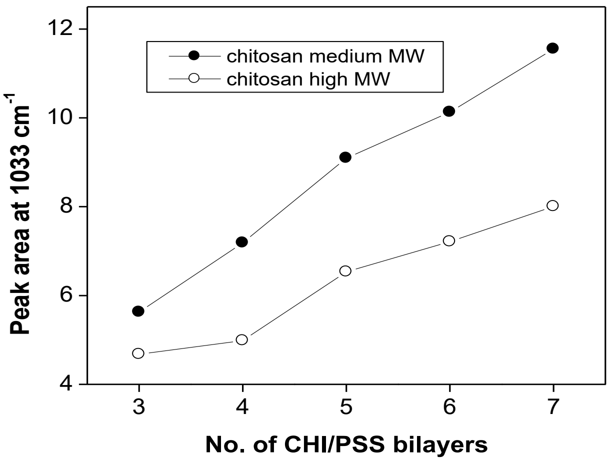


Fig. 5: The peak area at 1033 cm^{-1} in the FT-IR spectrum as a function of the number of bilayers when multilayers are fabricated from CHI (medium MW) /PSS and CHI (high MW) /PSS

On plotting the peak area at 1033 cm^{-1} in the FT-IR spectrum against the number of bilayers for multilayer system using two sets of chitosan, (fig. 5), it can be seen that there is appreciable variation in the peak area. This study shows that the efficiency of coating is better for medium molecular weight chitosan. Therefore, for further multilayer fabrication, medium molecular weight chitosan was selected.

4. CONCLUSION

It is possible to fabricate polyelectrolyte multilayers (PEM) on polyether sulfone supports by layer-by-layer assembly method. The multilayers could be characterized by SEM and FT IR spectroscopic methods. It was possible to fine tune the thickness of multilayer by varying parameters such as nature of the polymeric support, pH and molecular weight of the polyelectrolytes used.

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Conflicts of interest

Nil

6. REFERENCES

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