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Modification of a Membrane Surface Charge by a Low Temperature Plasma Induced Grafting Reaction and Its Application to Reduce Membrane Fouling

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ABSTRACT

A low temperature plasma was used to graft a positively charged monomer to initiate polymerization on a hydrophilic polysulfone membrane of negative surface charge. The surface modification was characterized by scanning electron microscopy and x-ray photoelectron spectroscopy. Changes in the membrane surface charge and ζ-potential before and after the modification were determined by measuring the electroosmotic flux across the membrane. The effects of the power, radiation time, and polymerizing reaction time on the modification were examined. Adsorption of positively charged lysozyme on the membrane modified with a positively charged monomer was much reduced due to reduced

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attractive electrostatic forces between lysozyme and the weaker negative charge of the modified membrane surface. Acrylic acid was also grafted as a monomer on the membrane and it gave an intensified negative surface charge. The adsorption of negatively charged bovine serum albumin (BSA) on the modified membrane was significantly reduced due to an enhanced electrostatic repulsive force between BSA and the acrylic acid modified membrane surface. The results show the important role of electrostatic forces in the interaction between protein molecules and a membrane surface, and that these can be controlled by the membrane synthesis or a surface modification to tailor the membrane to the needs of applications.

Key Words: Low temperature plasma; Microfiltration; Membrane modification; Surface charge; Bovine serum albumin; Lysozyme.

INTRODUCTION

There is rapid and growing interest in applying membrane technology to the downstream processing of biotechnology, drug delivery, and waste water treatment, in addition to its established applications in the industrial production of beverages and water.[1] The composition and structure of the membrane determine its performance.[2] The surface charge on the membrane is of great importance for its functioning in the separation process, especially for membrane apparatuses used with an electric field, e.g., forced flow electrophoresis,[3] recycle isoelectric focusing,[4] multichannel flow electrophoresis (MFE),[5] and those membrane spaced multicompartment electrolyzers. All these processes operate by the migration, driven by an electric field, of a charged component from one compartment to another.

An ideal membrane for these types of techniques should be hydrophilic to reduce protein adsorption by hydrophobic interaction. It should also be neutrally charged to prevent electroosmosis across the membrane. A major aim of the present study was to provide a neutral but hydrophilic membrane for preparative electrophoresis. A multicompartment electrolyzer originally designed for MFE was used to determine the electroosmotic flux across the membrane. The change in the surface charge in terms of the ζ-potential was calculated from the electroosmotic flux using the Smoluchowsky equation.[6]

The surface charge of the membrane was changed by the surface grafting of a charged polymer onto its surface. In general, membrane surface modification methods can be categorized into three major groups: (1) chemical reaction,[7] (2) photochemical reaction including UV[8] and γ-ray irradiation,[9]

and (3) low temperature plasma treatment.[10–13] The low temperature plasma treatment was first introduced by Yasuda[14] and has been widely accepted as a highly surface-selective modification method. Ulbricht[10] treated polyacrylonitrile and polysulfone membrane with water and He plasma. Surface hydrophilicity of treated membrane was drastically and almost permanently increased, thus giving a better protein UF performance. Chen[11] grafted *N*-vinyl-2-pyrrolidone onto a poly(ether sulfone) membrane surface through a plasma-induced graft polymerization reaction. The surface hydrophilicity of the membrane was increased and membrane fouling during bovine serum albumin (BSA) filtration was reduced. Steen[12] treated a polysulfone membrane with H_2O plasma. The hydrophilic modification was shown to be permanent, as the treated membrane remained wettable for more than 16 months. Kang[13] grafted acrylic acid and allylamine on a polypropylene membrane and determined the pH dependence of a BSA penetrating flux. In general, the enhancement of surface hydrophilicity was the major aim of studies using a low temperature plasma induced membrane surface modification.

In microfiltration and ultrafiltration processes in the downstream processing of biomolecules, membrane fouling, evident as a declining permeate flux caused by blocking of the membrane pores, is frequently observed. The approaches for overcoming this problem include back washing,[15] coupling with an electric field,[16] and using a specially designed membrane module to introduce additional turbulence.[17] Membrane surface modification has shown its unique advantage for understanding and reducing fouling at the molecular level.

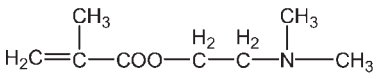
In our previous studies on protein adsorption on a membrane surface in an electric field, we observed an effect of the electrostatic force between the membrane and the protein molecules where protein adsorption was a function of pH.[18,19] Thus, it is of interest to understand the effect of the electrostatic interaction on protein adsorption on those hydrophilic membranes.

In the present study, a commercial hydrophilic polysulfone membrane, HT Tuffryn, was the membrane sample used for the low temperature plasma treatment, followed by the plasma-initiated graft polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA), C_4 monomer, and acrylic acid. Changes in the membrane surface were examined by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and the surface charge, expressed as the ζ-potential. Lysozyme and BSA, which have different isoelectric points, were the protein samples used to study membrane adsorption and filtration under different conditions and to look at the electrostatic interaction between the membrane and the protein molecules.

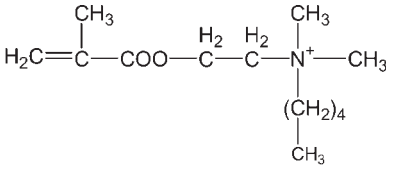
EXPERIMENTAL

Materials

Hydrophilic polysulfone membrane (HT), with a pore diameter of 0.45 μm and thickness of 0.12 mm, was purchased from Pall-Gelman Sciences (USA). 2-(dimethylamino)Ethyl methacrylate (DMAEMA) (a liquid at room temperature) was purchased from Aldrich Chemicals Co. (Milwaukee, USA) and used without further purification. The C_4 monomer, formula shown as follows, was synthesized by the Institute of Polymer Science of Tsinghua University. Acrylic acid was purchased from Acros (Geel, Belgium). BSA (fraction V) was the product of Roche (Basel, Switzerland), with a minimum purity of 98%. Lysozyme was the product of Sigma (St. Louis, US), with an activity of 5000 U/mg. Deionized water was obtained from a domestic water purification system. Other chemicals of analytical grade were purchased from standard suppliers.



DMAEMA



C_4 monomer

Plasma Treatment

A schematic diagram of the experimental system is shown in Fig. 1. The investigation was done in a cylindrical glass chamber 200 mm in length and 50 mm in diameter. All plasma experiments were excited with RF radiation matching network (13.56 MHz) (model SP-II, the Electronic Center, Chinese Academy of Science, Beijing, China). The vacuometer was purchased from Chenghua Electronic Instrument Factory, Chengdu, China. During a run, the system was first filled with argon and evacuated to a vacuum of 15 Pa. A plasma was generated by the application of electric power for a given time. For the grafting of DMAEMA and the acrylic acid monomer, the monomer vapor was introduced for reaction with the membrane sample after the plasma generation step. After polymerization, the vacuum was replaced by air. The membrane sample was then taken out and soaked in deionized water for more than 12 hr, with the water changed at intervals to remove impurities before subsequent measurements.

For the grafting of the C_4 monomer, the membrane was taken out after the plasma treatment, soaked in 5 wt% C_4 solution, and incubated at 50°C for 1 hr

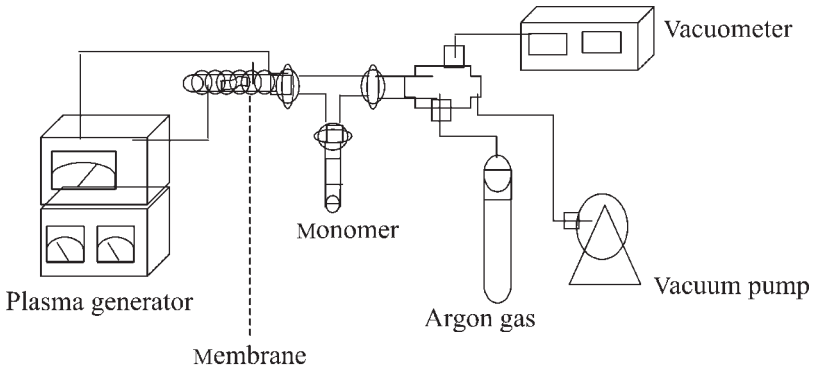


Figure 1. Schematic diagram of the apparatus used for plasma modification.

for the polymerization reaction. The sample was then soaked in deionized water as described previously.

Surface Characterization

SEM pictures were obtained using a Hitachi S450 microscope (Tokyo, Japan). Membranes were cut into tiny pieces and then, a thin gold film was sputtered onto the membrane surface prior to SEM observation.

XPS analysis was performed using a Physical Electronics PHI5300 spectrometer (Eden Prairie, MN, USA). The composition was determined from 0 to 1000 eV survey scans. The O_{1s}, C_{1s}, N_{1s}, and S_{2s}, S_{2p} spectra were collected and subjected to atomic concentration analysis.

Electroosmosis Measurement and BSA Filtration in a MFE Apparatus

In a previous study on MFE, we showed that the ζ-potential is highly sensitive to membrane fouling.[18] The ζ-potential of the original and modified membranes was determined by measuring the electroosmotic flux in an apparatus. The MFE separation apparatus is described in detail in Ref.[5] The heart of it is a five-chamber electrolyzer, shown in Fig. 2. The length and width of each chamber are 120 and 10 mm, respectively. The depths of the electrode, elution, and central chamber are 4, 2.5, and 2.5 mm, respectively. Polyacrylamide gel membranes were placed between chambers 1 and 2 and between

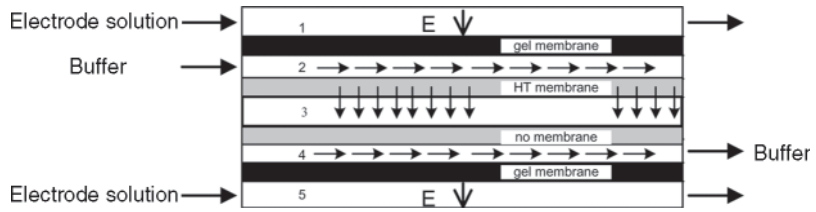


Figure 2. Schematic diagram of the apparatus used for electroosmosis measurements.

chambers 4 and 5. The HT membrane (original or modified) was placed between chambers 2 and 3.

During the measurement, phosphate buffer solution of high concentration was circulated in the two-electrode chambers. A dilute phosphate buffer solution of identical pH was loaded into chamber 2 by hydrostatic pressure, penetrated across the membrane, and was collected at the outlet of chamber 4. Once an electric field was applied vertically, the electroosmotic flux across the HT membrane led to an increase or decrease in the outlet flux obtained from chamber 4. The polarity and magnitude of the ζ-potential of the HT membrane was determined by the Smoluchowsky equation.[6]

$$J_v = \frac{\varepsilon_r \varepsilon_0 \zeta I}{\eta \kappa}$$

where J_v is the electroosmotic flux, ε_0 is the permittivity of vacuum, ε_r is the relative dielectric constant of the buffer, η is the viscosity of the buffer, and κ is the electroconductivity of the buffer. Unless stated otherwise, phosphate buffer solution of pH 7.0 was used throughout this study. The electroconductivity, which is an index of the ionic strength, of the electrode buffer and loading buffer were 8200 and 400 μm/cm, respectively.

BSA filtration was also carried out in the MFE apparatus without an electric field. The flow pattern inside the apparatus was the same as that in the measurement of the electroosmotic flux. The concentration of the BSA solution was 1 mg/mL. The flux at the outlet was measured gravimetrically.

Static Protein Adsorption Experiment

Yin and colleagues[19] found that the adsorption of human serum albumin (HSA) on the HT membrane was complete within a few minutes. In the present study, the original and modified HT membranes were soaked in a protein solution of the given concentration for 1 hr to ensure a sufficient adsorption

time. The ζ-potentials of the membranes before and after protein adsorption were determined using the method described previously.

RESULTS AND DISCUSSION

Characterization of the Modified HT Membrane

SEM photos of the HT membrane modified with DMAEMA monomer are shown in Fig. 3. This shows that the surface morphology of modified membrane has not been much altered. However, an extended treatment time by low temperature plasma leads to a small increase in the number of big pores. This may attribute to the breaking and rearrangement of the polymer network of the membrane surface by the plasma.

It is commonly accepted that plasma treatment is confined to the top several tens of nanometers and it is not expected to affect the bulk polymer properties.[11,20] In our study, we could hardly measure the change of weight of membrane after modification, by a 0.1-mg electronic balance. XPS is highly surface sensitive and can provide information on the atomic concentration and binding state, with a usual sampling depth of several nanometers. So this technique is frequently used in the plasma treatment study. Figure 4 shows the XPS spectra of the original and DMAEMA-modified HT membrane. A nitrogen peak is identified in the modified membrane. Since the original HT membrane contains C, H, O, and S only, the presence of nitrogen must be due to the low temperature plasma-induced graft reaction of the DMAEMA monomer.

As shown by the results listed in Table 1, an increase in the nitrogen concentration in the modified HT membrane results from a longer treatment time or an increase in the plasma generating power. However, when the treatment time exceeds 120 sec, there is no further increase in the nitrogen concentration as the treatment time is further increased.

Effects of Plasma Treatment on the ζ-Potential of the Modified HT Membrane

The effects of the plasma treatment time and plasma generating power on the ζ-potential of the DMAEMA-modified HT membrane were examined at a graft polymerization time of 10 min. It can be seen in Fig. 5 that the magnitude of the ζ-potential decreases with increased plasma treatment time. When the treatment time exceeds 120 sec, no further decrease in the magnitude of the ζ-potential was observed. This is in agreement with the data in Table 1.

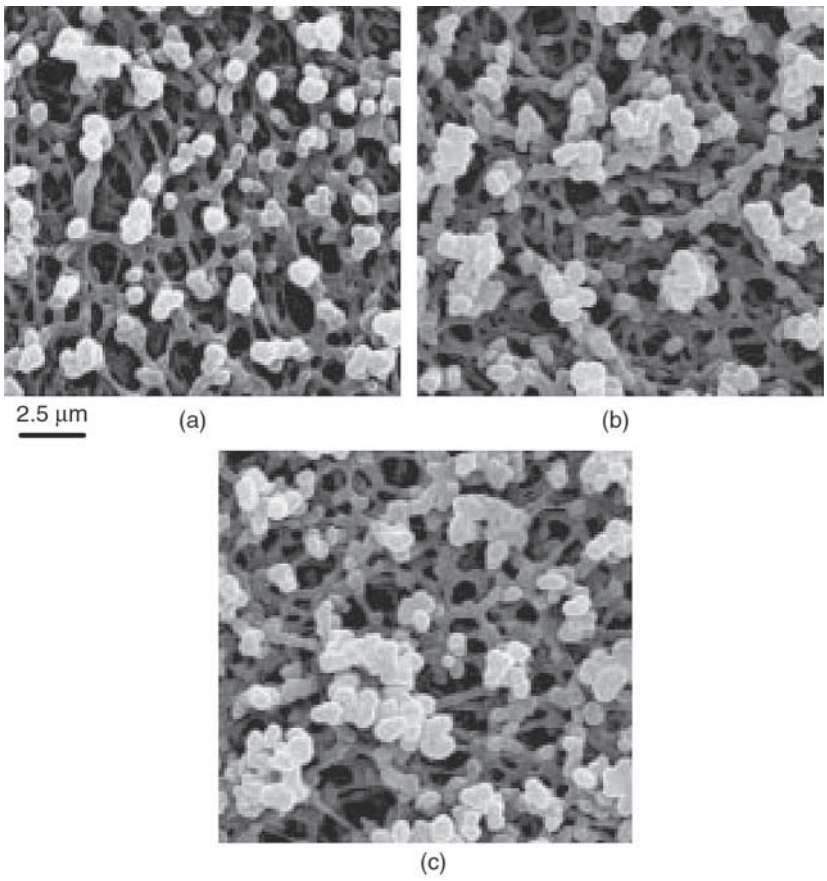


Figure 3. SEM photos of the original and DMAEMA-modified HT membranes. (a) Original HT membrane; (b) experimental conditions: $T_1 = 60$ sec, $T_2 = 10$ min, $P = 40$ W; (c) experimental conditions: $T_1 = 180$ sec, $T_2 = 10$ min, $P = 40$ W. T_1 is the plasma treatment time, T_2 is the grafting and polymerization time, and P is the plasma treatment power.

The observation that the further increase in the plasma treatment time contributes little to the surface modification is reported elsewhere.[10,12,20] However, the mechanism has not been clarified. It is possible that at the beginning stage, more active sites are made available for the grafting reaction by an increase in the treatment time. However, beyond a certain treatment time (120 sec in the experiments here), the further increase in the treatment time may lead to membrane surface etching and the loss of active sites.[10]

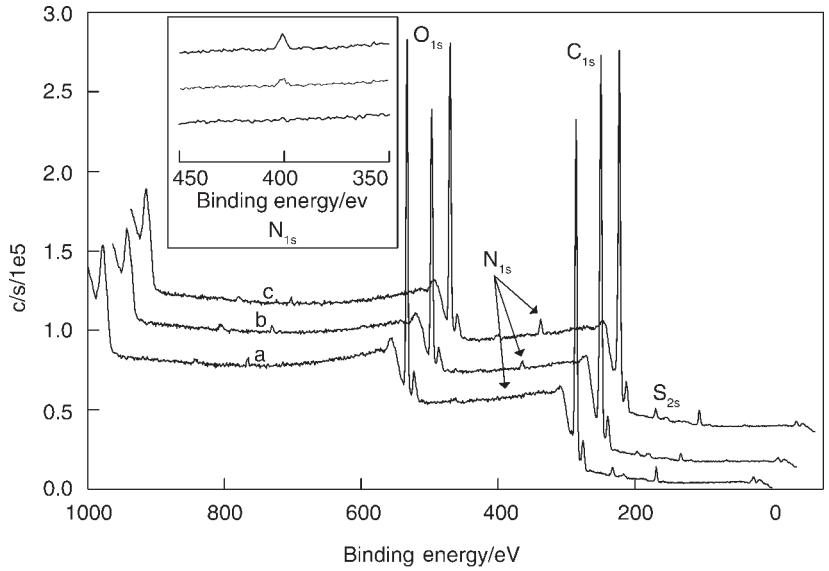


Figure 4. XPS spectra of (a) original membrane; (b) DMAEMA-modified HT membrane, $T_1 = 60$ sec, $T_2 = 10$ min, $P = 20$ W; and (c) DMAEMA-modified HT membrane, $T_1 = 120$ sec, $T_2 = 10$ min, $P = 40$ W.

Surface etching can also be demonstrated by flow resistance experiments, and is discussed in the following section. It is also possible that steric hindrances by grafted DMAEMA above a certain concentration prevents the access of DMAEMA monomer to the membrane surface and inhibits the grafting and polymerization reaction.

In Fig. 5, the treatment power is 20 and 40 W. Thus, we could estimate the energy needed for plasma treatment by the product of treatment power and

Table 1. Elemental concentration of the original and DMAEMA-modified HT membranes (%).

Sample	C	O	S	N
Original HT	71.92	26.89	1.19	—
$T_1 = 60$ sec, $T_2 = 10$ min, $P = 20$ W	70.96	27.32	1.06	0.67
$T_1 = 60$ sec, $T_2 = 10$ min, $P = 40$ W	78.61	19.75	0.63	1.01
$T_1 = 120$ sec, $T_2 = 10$ min, $P = 40$ W	72.17	24.27	1.42	2.14
$T_1 = 180$ sec, $T_2 = 10$ min, $P = 40$ W	70.88	25.61	1.31	2.20

T_1 refers to plasma treatment time, T_2 refers to polymerization time.

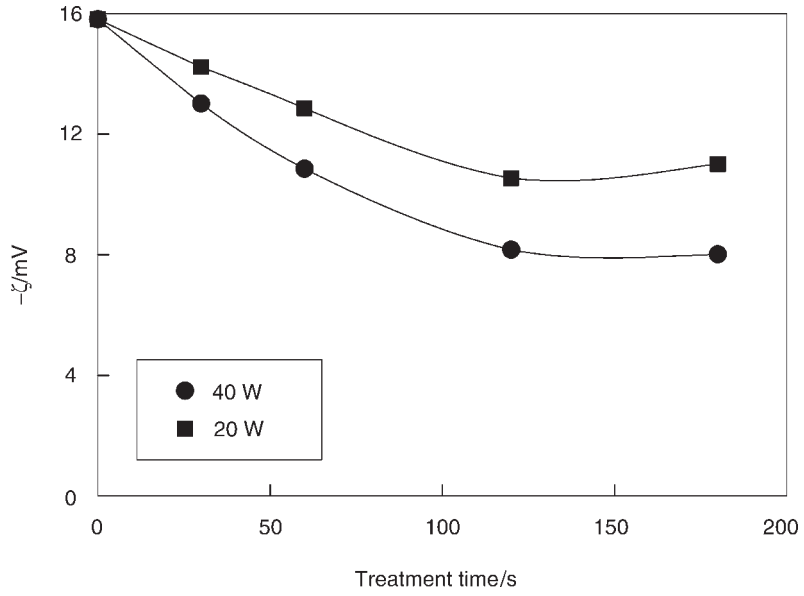


Figure 5. Effect of plasma treatment on the ζ-potential of a DMAEMA-modified HT membrane.

treatment time. In our study, 4500–5000 J is the minimum energy needed to give a considerable modification effect.

Effect of the Graft Polymerization Time on the HT Surface Modification

The HT membrane samples were first subjected to the plasma reaction at a power input of 40 W for 2 min. Then, the DMAEMA monomer vapor was introduced into the reaction system for a different time to examine the effect of the grafting and polymerization time on the ζ-potential of the modified HT membrane.

It can be seen from Fig. 6 that the ζ-potential of the modified membrane is not much affected by the graft polymerization time. This may be due to the fact that the number of active sites available for reacting with the DMAEMA is determined by the total plasma input, which is a function of the power input and radiation time. It is also possible that surface grafting and polymerization is a fast reaction and the available sites are quickly

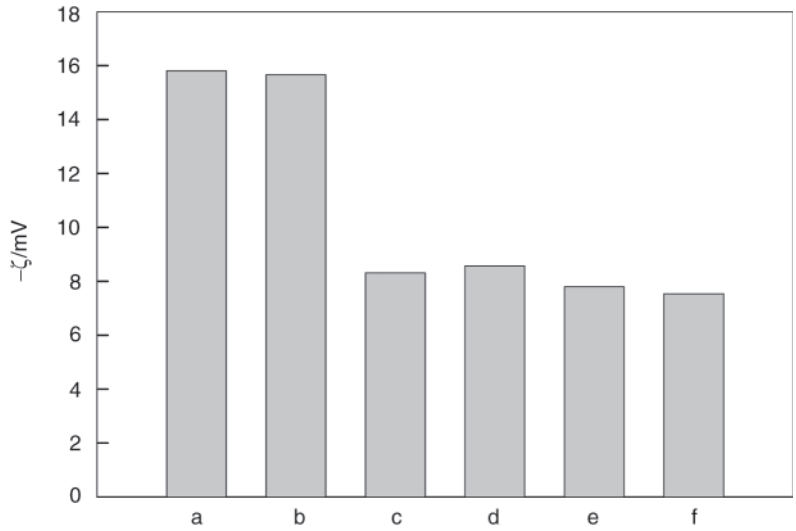


Figure 6. Effect of grafting and polymerization time on the ζ-potential of a DMAEMA-modified HT membrane. (a) Original HT membrane; (b) plasma-modified HT (without grafting and polymerization); and (c) through (f) grafting and polymerization time of 2, 5, 10, 15 min, respectively.

occupied by DMAEMA. In any event, a longer polymerization time contributes little to the surface modification.

When the HT membrane is subjected only to plasma treatment, as shown in the case of sample b, the ζ-potential is close to that of the original membrane. This indicates that a plasma treatment process in argon has little effect on the surface charge of the membrane. Thus, a change in the surface charge has to be due to the grafting of charged groups.

pH Sensitivity of the ζ-Potential of the Modified Membrane

The DMAEMA monomer is a tertiary amine compound and can be protonated in a buffer solution to form a positively charged quaternary ammonium compound. The C_4 monomer is a quaternary ammonium salt that can be grafted onto the membrane surface as a cation. Figure 7 shows the ζ-potentials of the original and modified membranes as a function of the buffering pH. It can be seen that the ζ-potential of the original membrane is not much changed by the buffer pH, while the ζ-potential of the DMAEMA-modified HT is dramatically decreased in response to a decrease

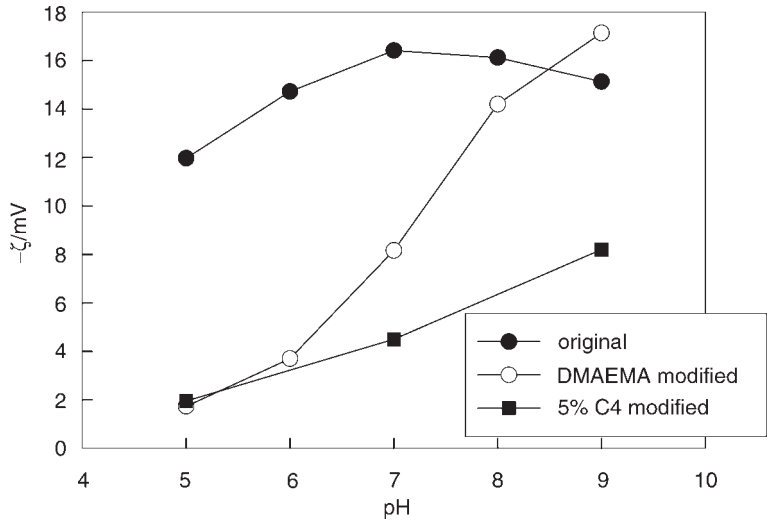


Figure 7. Effect of pH on the surface ζ-potential of the DMAEMA- or C4-modified HT membrane. Experimental conditions of DMAEMA modification: $P = 40\,\mathrm{W}$, $T_1 = 120\,\mathrm{s}$, $T_2 = 10\,\mathrm{min}$.

in the pH. The different responses to the pH are also evidence of the grafting of DMAEMA on the HT surface. The negative surface charge of the HT membrane can be better neutralized by the C_4 monomer modification, as the positive charge of the C_4 monomer is larger than that of the DMAEMA. The pH response of the C_4-modified HT membrane is not as marked as that of the DMAEMA-modified membrane. The sensitivity of the surface charge, in terms of the ζ-potential, to the pH provides the possibility for enhancing microfiltration or ultrafiltration through charge rejection, in addition to rejection based on molecular size and shape.

Flow Resistance of the Modified Membrane

The penetration flux across the original and DMAEMA-modified HT membrane was determined as a function of the pressure drop, with different plasma treatment time and the same graft polymerization time of 10 min. As shown in Fig. 8, a slight increase in the flux in response to an increase in treatment time results in the case of the modified membrane. This may indicate the occurrence of membrane surface etching. This suggests that the treatment time or plasma generating power may affect the pore size and that they

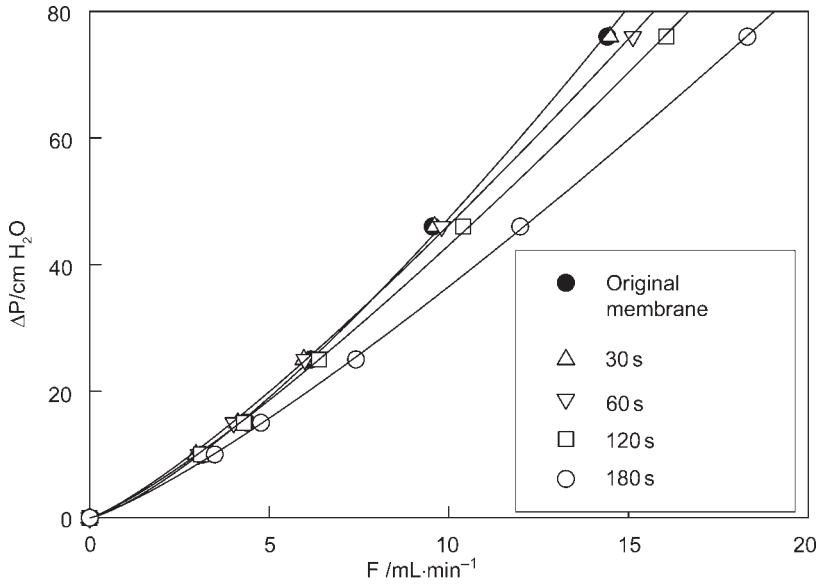


Figure 8. Flow resistance of the original and DMAEMA-modified HT membrane with different plasma treatment times.

should be chosen with care to maintain the expected size rejection property of the membrane.

Fouling Characteristics of the Modified Membrane

Wang[18] and Nyström[21] showed that the adsorption of charged biomolecules leads to a corresponding change in the ζ-potential. Thus, we can use the ζ-potential to characterize membrane fouling. In the present study, the original and DMAEMA-or C_4-modified HT membranes were first soaked in BSA (10 mg/mL, pH 7.0) and lysozyme (1 mg/mL, pH 7.0) solution, respectively, before the measurement of the electroosmotic flux with the method described previously. The results are shown in Fig. 9.

The results in Table 2 show that the ζ-potential of the original HT membrane is almost the same before and after BSA adsorption. In the case of soaking in lysozyme, a large change in the ζ-potential of the original HT membrane was observed, indicating the adsorption of lysozyme on the HT surface.

The HT membrane used in present study is characterized by low protein adsorption[19] and a strong negative surface charge. Thus, the difference in protein adsorption is mainly due to the fact that BSA (pI 4.9) is negatively

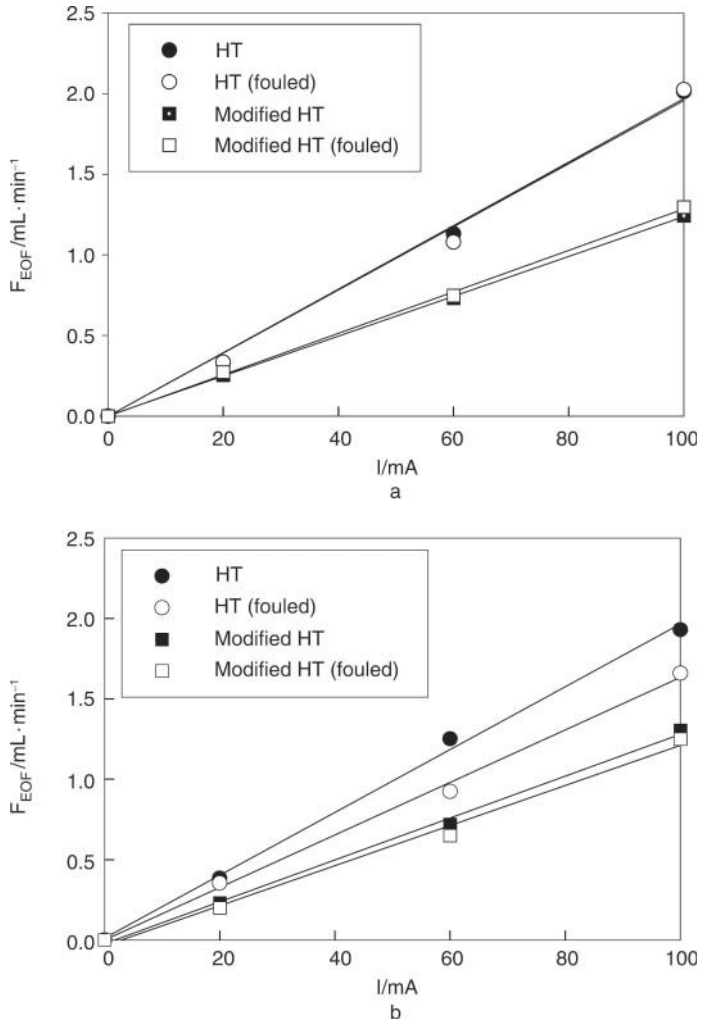


Figure 9. Electroosmosis flux across the membranes before and after protein adsorption at pH 7.0. (a) BSA; and (b) lysozyme. Membrane modification conditions: $P = 40$ W, $T_1 = 120$ sec, $T_2 = 10$ min, with DMAEMA as the monomer.

charged at pH 7.0, while lysozyme (pI 10.5) is positively charged at pH 7.0. The consideration of the electrostatic force indicates that they would interact in different ways with the negatively charged HT membrane. An attractive electrostatic force favors the adsorption of lysozyme, while a repulsive

Table 2. ζ-Potential change of the membranes after protein adsorption at pH 7.

Membrane	ζ-Potential of membrane (mV)	Change of ζ-potential after BSA adsorption (mV)	Change of ζ-potential after Lys adsorption (mV)
HT	−16.2	−0.023	+2.40
DMAEMA-modified HT	−7.8	−0.200	+0.38
C4 modified HT	−4.5	−0.140	+0.30

electrostatic force reduces BSA adsorption. Yin and co-workers[22] and Stuart and colleagues[23] also showed that electrostatic forces may be the major driving force in protein adsorption.

Due to the introduction of a positively charged polymer, the magnitude of the ζ-potential of the DMAEMA-modified HT membrane decreased by about 50% at pH 7.0. In the case of the C_4 monomer-modified membrane, the net negative charge can be further decreased to about one-fourth of the original membrane at pH 7.0. As a result, the attractive electrostatic force between lysozyme molecules and the modified membrane are also reduced, compared with the original HT membrane. Also it can be seen from Table 2 that the shift of the ζ-potential after lysozyme adsorption is +0.38 mV in the case of the DMAEMA-modified membrane, +0.30 mV in the case of the C_4-modified membrane, and +2.4 mV in the case of the original HT membrane. This indicates a dramatic decrease in the adsorption of lysozyme on the modified membranes.

HT Membrane Modification with Acrylic Acid as the Monomer

Acrylic acid has been widely used to increase surface hydrophilicity in membrane modification study. Both Wavhal[24] and Xu[25] grafted acrylic acid monomer onto polyethersulfone and polypropylene membrane. Their investigations mainly focused on the effect of surface hydrophilicity increase on membrane fouling. While in our study, the introduction of acrylic acid onto the HT membrane was aimed at enhancing its negative charge by the release of H^+ ions into solution. The ζ-potential of the acrylic acid modified HT membrane was determined by measuring the electroosmotic flux. The results are shown in Fig. 10.

BSA filtration on the acrylic acid modified HT membrane was carried out in the absence of an electric field. The results are also shown in Fig. 10. The

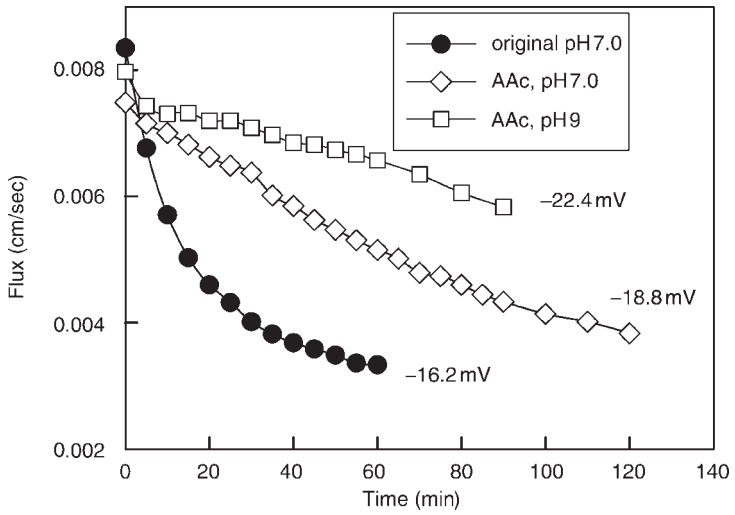


Figure 10. BSA filtration using the original and acrylic acid (AAc)-modified HT membrane. Modification conditions: $P = 40\,\text{W}$, $T_1 = 120\,\text{sec}$, $T_2 = 10\,\text{min}$. The ζ-potentials of these membranes are also shown in the figure.

BSA penetrating flux continuously decreased during the filtration process. However, in the case of the acrylic acid modified HT membrane, the reduction rate of the penetrating flux was significantly reduced. This is mainly due to an enhanced repulsive electrostatic force that hinders the adsorption or deposition of BSA molecules onto the membrane surface. An even better filtration is possible at pH 9.0, compared with that at pH 7.0, as a result of the enhanced repulsive electrostatic forces between BSA and the modified HT membrane, cause the negative charge of BSA molecule and modified HT membrane at pH 9.0 are both larger than those at pH 7.0.

Hydrophobic interaction and electrostatic force are the two major causes of membrane fouling. In membrane separation or the concentration of protein from its aqueous dilute solution, a hydrophobic interaction is often the major cause of membrane fouling. Thus, much effort has been exerted to make the membranes hydrophilic. In the present study, we have shown the effect of attractive or repulsive electrostatic forces on protein adsorption on a commercial hydrophilic membrane surface, and shown that a modification of the membrane surface charge by the introduction of a polymer with the correct charge properties using a low temperature plasma can be applied to cope with the membrane fouling problems. The modification of the membrane surface charge has also applications in membrane apparatuses that operate in an electric field.

The important role of electrostatic interaction in many filtration processes has been demonstrated but few methods are available for the quantitative analysis of this effect. Menon and Zydney[26] have developed the so-called "protein charge ladders," which are a series of chemical derivatives of a given protein that differ by single charge units, to study electrostatic interaction during ultrafiltration. In our study, we fabricated a series of membranes with almost similar morphology but different charge properties, which could be so-called "membrane charge ladders." More efforts should be addressed to the quantification of the interaction between the protein molecule and the membrane surface.

In addition, molecular simulation is an important and complementary approach to experiments. A visual description of the protein interaction with the membrane surface at a molecular level will provide a powerful tool for membrane design, membrane surface modification, and the implementation of membrane-based processes.

CONCLUSION

A commercial polysulfone membrane was modified by grafting a charged polymer onto it using a low temperature plasma. The effects of the plasma treatment time, plasma generating power, and polymerization time on the pore structure, chemical composition, and ζ-potential of the modified membrane surface were examined. The static adsorption of BSA and lysozyme on a DMAEMA- or C_4 monomer-modified HT membrane and the filtration of BSA through an acrylic acid modified HT membrane showed that the enhancement of the repulsive electrostatic force was effective in reducing protein adsorption on the membrane surface. The results show the role of electrostatic forces in membrane fouling and can be used to guide membrane synthesis and membrane surface modification.

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