ANTITHROMBOGENICITY OF NANO POROUS POLYETHERSULFONE MEMBRANE COATED WITH FLUORINATED DIAMOND-LIKE CARBON

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ABSTRACT

We have ever developed micro dialysis system that consists of micro channels and polyethersulfone (PES) membranes. However, when blood was used in dialysis experiments, platelets adhered to the surface of membrane and performance of the membrane degraded. Therefore, we modify the surface of PES membranes by coating fluorinated diamond-like carbon (F-DLC). We examined antithrombogenicity of the F-DLC/PES membranes using a microfluidic device and experimentally found that F-DLC drastically reduced the amount of cells attached to the surface. We conducted long-term experiments for 1 week and the diffusion characteristics were found to retrogress because of fouling without the surface modification.

KEYWORDS: ano porous polyethersulfone membrane, Fluorinated diamond-like carbon, Dialysis system

INTRODUCTION

Nano porous polyethersulfone (PES) membrane is a promising material for nanofiltration such as purification, fractionation and dialysis due to its high mechanical, hydraulic stability, thermal and chemical resistance. In spite of such as good properties of PES membrane, platelets or protein tend to adhere to the surface of PES membrane and diffusion of ions through the membrane degraded when they were used in blood contact devices as illustrated Figure 1 [1]. Therefore it is necessary to modify the surface of PES membranes. To approach the multi applications, numerous researches have been carried out to modify PES membranes, such as blending, surface physical treatment, surface grafting and coating etc.

In this work, we explain that the surface modification of PES membrane by deposition of fluorinated diamond-like carbon (F-DLC) film. F-DLC is a material adding fluorinate to diamond-like carbon (DLC) and has been widely used as a coating material in blood contacting devices, due to its antithrombogenicity [2]. F-DLC film was prepared using radio frequency (RF) plasma enhanced chemical vapor deposition (CVD) method. However it is impossible to coat F-DLC on top side layer of PES membrane called skin layer without clogging the porous because PES is a semipermeable membrane which has two layers, skin layer and porous layer and skin layer is a nano porous as illustrated Figure 2. For that reason, we applied the F-DLC coating to the porous layer. During the F-DLC coating process, the F-DLC gas could easily goes through to the micro porous and then deposited on the structure of the porous layer like Figure 3. Hence, we have the F-DLC film covering the structure of the porous layer and keeping the nano porous opened. Thus we investigated the effect by coating F-DLC on PES membranes.

EXPERIMENTAL

A. Materials

PES membranes were made from PES (molecular weight: 4800, Sumitomo Chemical Co., Japan), polyvinylpyrrolidone (PVP) (molecular weight: 35000, Wako Pure Chemical Industries, Ltd., Japan), and 1-methyl-2-pyrrolidone (NMP, Wako Pure Chemical Industries, Ltd., Japan), acting as solute, solvent and additive, respectively. PES membranes are blended the PES, PVP and NMP at 20%, 20% and 60% (wt%), individually, and kept at room temperature for about 24 hours to form transparent casting solutions. Thereafter, the PES casting solution was poured onto a glass sheet. Then the PES membrane was prepared using spin coating at a spinning speed of 3000 rpm followed by direct immersion into distilled water. Then formed PES membranes were conserved in distilled water for at least 24 hours at the room temperature to remove the PVP completely and in a uniform thickness about 100 μm.

Figure 1: Dialysis using PES membrane and platelets adhered to its surface

Figure 2: the cross section of PES membrane
B. Membrane modification

Conventional F-DLC film was prepared on substrates which are the PES membranes using RF plasma enhanced CVD method by changing the ratio of hexafluoroethane (C$_2$F$_6$) and acetylene (C$_2$H$_2$) at 60% and 40% of total pressure. The RF (13.56 MHz) power and total pressure were fixed at 200 W and 13.3 Pa, respectively. Thus F-DLC films were deposited on the porous layer (bottom side of PES membrane).

C. SEM image analysis

In this study, 5.5 nm, 6 nm and 7.7 nm of F-DLC thickness were deposited on PES membrane. We observed the surface of them in the scanning micrograph images (SEM) to confirm F-DLC film because its thickness was very thin such as about 3~7 nm.

D. Diffusion test experimental

For diffusion test, we designed and assembled the miniature of hemodialysis system (Figure 5). Diffusion tests were conducted by feeding blood and dialysate into dual inlet of the chamber, hence molecule smaller than the mean pore size of the membrane can diffuse through the membrane. The diffusion tests were also conducted in different two types of diffusion, short and long term diffusion test. Short term diffusion (2 hours) test was performed by using single pass system as shown Figure 5(b) to examine blood compatibility of PES and F-DLC/PES membranes. After this test, we have checked surfaces of PES and F-DLC/PES membrane in SEM.

On the other hand, long term diffusion test was performed by using roop system as shown Figure 5(c) to evaluate the membrane permeability in 1 week. At this point, we introduced the diffusion coefficient $D_c$ [$m^2/s$] of a solute as an index of permeability [3,4]. The $D_c$ was determined based on the following equation;

$$D_c = \frac{QH}{A} \ln \frac{C_{B,in} - C_{B,out}}{C_{A,in} - C_{A,out}}$$

Where $Q$ is the flow rate [$m^3/s$], $H$ the membrane thickness [$m$], $A$ the channel area [$m^2$], $C$ the concentration [$M$], $A,B$ the solution type, and $in$, $out$ the inlet/outlet. Thus, we can calculate the $D_c$ by measuring the concentration of solutions.
RESULTS AND DISCUSSION

A. SEM image analysis

Figure 4(c) shows some micro pores of PES membrane were coated with F-DLC. It is confirmed that F-DLC film has been coated on the PES membrane. Moreover, we could find that 7.7 nm F-DLC film has completely covered the membrane porous, therefore only membrane coated with 5.5 nm and 6.6 nm of F-DLC films were examined in the diffusion test.

B. Short term diffusion test

Figure 6 shows the SEM images and the number of blood cells adhere to the membrane surfaces after short term diffusion test. It could be observed that numerous blood cells accumulated and coagulated on the PES membrane surface. However, very sparse blood cells were observed for F-DLC/PES membranes. This should be attributed to the antithrombogenicity of F-DLC coated on the PES membrane.

C. Long term diffusion test

Figure 7 shows the diffusion coefficient of the membranes, where the PES membrane gave the highest diffusivity, followed by 5.5 nm and 6.6 nm of F-DLC film thickness. However, when the experiments were continued to 7 days, the three membranes gave similar diffusion coefficient. It could be found that the diffusion coefficient of PES membrane got worse while ones of F-DLC/PES membranes were steadied.

CONCLUSION

In this study, we described an antithrombogenic effect by coating PES membrane with F-DLC. The number of blood cells decreased in order of the PES membrane, F-DLC (5.5 nm)/PES membrane, F-DLC (6.6 nm)/PES membrane. In the long term diffusion test, it showed that F-DLC/PES membranes were a relatively consistent in the diffusion coefficient. The coated F-DLC appears to be a promising candidate coating material for semipermeable membrane in the hemodialysis system.

REFERENCES


