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REVIEW OF SURFACE MODIFICATION OF NANOPOROUS POLYETHERSULFONE MEMBRANE AS A DIALYSIS MEMBRANE

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ABSTRACT

Nanoporous polyethersulfone (PES) membrane is widely used as a filtration membrane in hemodialysis systems. Unfortunately, it has low blood compatibility, and induces blood clots that adhere to the membrane's surface during dialysis treatment. This paper reports on a review of surface modification that is used to improve the PES membrane's blood compatibility. The method consists of applying two coating materials, in the form of parylene and fluorinated diamond-like carbon (F-DLC) films, onto the membrane's surface. The parylene film is deposited on the diffusion layer of the membrane surface using glycerin liquid, while the F-DLC film is specially coated on the supporting layer of the membrane. The unique property of parylene, which has the characteristics of conformal coating, prevents the parylene from being coated on the supporting layer of the membrane. Conversely, F-DLC film, which is hard, fragile and has a less conformal coating than parylene, is only meant to be coated on the supporting layer. Finally, the coated membranes, along with the bare PES membrane, are compared and investigated under a long-term diffusion test to assess their permeability and blood compatibility. The experiment results show that both coating materials have the capacity to improve the membrane's blood compatibility in different ways.

Keywords: Fluorinated diamond-like carbon; Hemodialysis; Parylene film; Polyethersulfone membrane

1. INTRODUCTION

In Indonesia, more and more people are suffering from kidney failure in recent years. According to data released by PT Askes Indonesia, the number of patients reached 24,141 in 2012 from 23,261 patients in 2011 (Pernefri, 2014). Kidney failure is a condition whereby the kidneys fail to sufficiently remove waste products from the blood (National Institute of Health, 2012). One of the options for treatment is dialysis (Suja et al., 2012), which performs the function normally carried out by kidneys: keeping the human body in balance by filtering and removing waste and salt to prevent them from accumulating in the body. A dialysis system uses a semipermeable membrane known as a dialysis membrane, which keeps the blood separate from the dialysate in order to remove excess waste. Polyethersulfone (PES) membrane is one of the semipermeable membranes used in this system, due to its extraordinary properties; it can be easily fabricated at room temperature (Gu & Miki, 2007). In addition, the nano porosity of the

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PES membrane makes it highly effective in filtering wastes from the blood (Prihandana et al., 2012).

The disadvantage of PES membranes is that they possess low blood compatibility, which has prevented their widespread application in dialysis treatment (Liu et al., 2009). Researches have been conducted to address this shortcoming; one method is to modify the membrane's surface. Recently, paryelene film and fluorinated-diamond-like-carbon (F-DLC) have become well known as two of the best coating materials for medical tools, due to their outstanding blood compatibility and conformal coating properties (Noh et al., 2004; Saito et al., 2005). However, such conformal coating characteristics can also become a problem if these materials are directly deposited on the membrane surface.

This paper reviews the modification techniques used on these materials in order to have them properly deposited on the membrane surface. A long-term diffusion test was conducted to validate the permeability and blood compatibility of parylene and F-DLC films in this application.

2. EXPERIMENTAL SETUP

2.1. Membrane Preparation

PES membranes were prepared from PES powder (molecular weight: 4800, Sumitomo Chemical Co., Japan), polyvinylpyrroli-done (PVP; molecular weight: 35,000, Wako Pure Chemical Industries, Japan), and 1-methyl-2-pyrrolidone (NMP; Wako Pure Chemical Industries, Japan), as solute, solvent, and additive components, respectively. PES, PVP, and NMP were mixed in a ratio of 20: 20: 60 (wt %), respectively, and kept at room temperature for approximately 48 h to form a transparent casting solution.

The PES solution was then poured onto a glass substrate. The PES membrane was then prepared by spin coating, followed by direct immersion into distilled water. As soon as the glass substrate was immersed in distilled water, a thin layer of white membrane appeared, forming at the interface between the casting solution and the distilled water. The as-formed PES membranes were then stored for further use in distilled water at room temperature for more than 24 h to remove the PVP solvent.

2.2. Membrane Modification

2.2.1. Parylene surface modification

A surface modification technique for depositing parylene-C onto the PES membrane was developed by using a Labcoater 2 Parylene Deposition Unit (SCS Coating Center Parylene Japan, LLC) (Prihandana et al., 2012). The deposition was accomplished by utilizing the passage of glycerin vapors through the membrane in order to create a nanoporous parylene film. During the deposition process, the glycerin vaporizes and passes through the membrane pores, preventing parylene deposition above the pores and subsequent blocking. In this experiment, 10 mg of parylene dimer was used in order to attain a parylene film thickness of 5 nm on the membrane surface.

2.2.2. F-DLC surface modification

We modified the deposition technique of F-DLC films by depositing them on the finger-like structure layer of the PES membrane, rather than employing glycerin liquids (Prihandana et al., 2013). This technique aimed to have the F-DLC film adhere to the wall of the porous membrane, rather than being deposited on its surface.

The finger-like structure has a greater porousness than the diffusion layer; therefore, it would be easier for the F-DLC film to go through the inside of the porous membrane and be deposited on

the wall. In this experiment, the deposition time of F-DLC film was 6 seconds, which yielded a film thickness of approximately 6 nm.

2.3. Diffusion Test Experiment

A diffusion test was conducted in order to observe the blood compatibility of the membrane before and after the deposition process. A diffusion chamber was made using a polymethylmethacrylate plate. The tested membrane was clamped between the blood and dialysate inside the diffusion chamber. Gas-tight syringes (Hamilton Company, USA) were used to pump the blood and dialysate to the diffusion chamber, as illustrated in Figure 1.

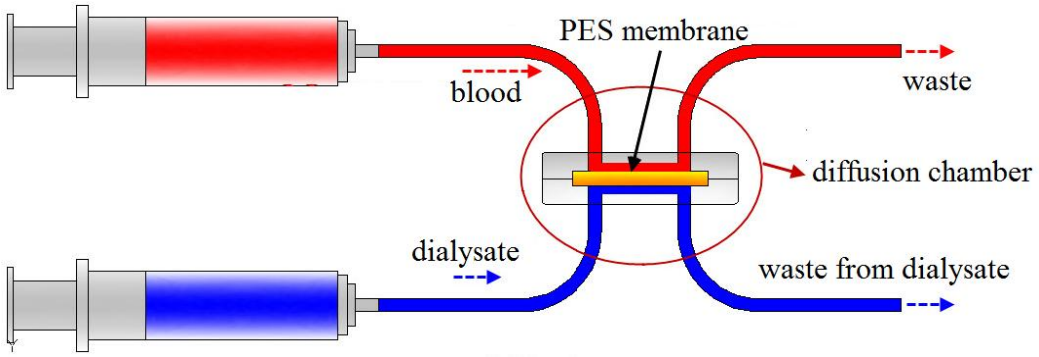

Figure 1 Diffusion test setup (Prihandana et al., 2014)

In addition to the diffusion test setup, the blood and dialysate solution was used as a fluid medium for solute transport. Defibrinated bovine blood was used as a blood solution, and a NaCl and K solution, which met medical standards, was used as a dialysate solution (Prihandana et al., 2014).

3. RESULTS AND DISCUSSION

3.1. Deposition of Parylene Film

A specific deposition method was developed to have the parylene film coated on the membrane surface without clogging the porous membrane (Prihandana et al., 2012). In this process, parylene was deposited on the diffusion layer of the PES membrane, using glycerin liquid. Having glycerin liquid placed under the membrane during this process avoided the parylene gas being deposited on the porousness of the membrane.

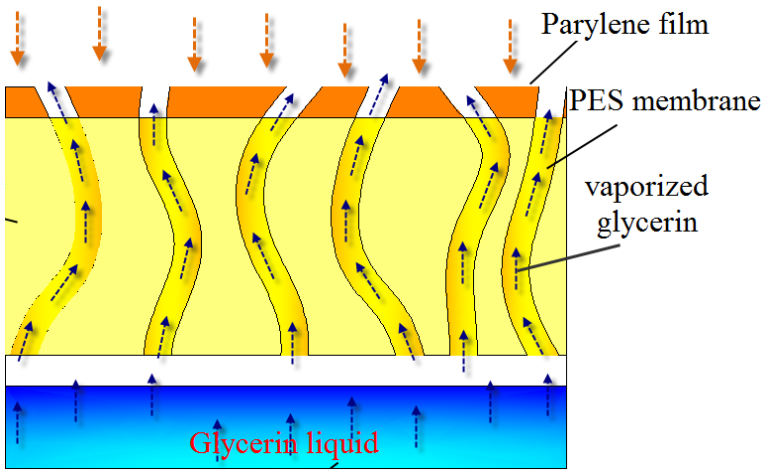

Figure 2 Parylene deposition employing glycerin vapors (Prihandana et al., 2012)

The glycerin was vaporized during the deposition process, due to its low vapor property. The vaporized glycerin went through the porous membrane to prevent the parylene from being deposited on it, as illustrated in Figure 2. Therefore, we obtained a higher diffusion coefficient of the solutes through the membrane, compared to the conventional parylene deposition process.

3.2. Deposition of F-DLC Film

F-DLC film has a different physical appearance than parylene film; it is harder and more brittle. Therefore, glycerin liquid could not be used, in contrast to the parylene deposition process. For this reason, we decided to coat the F-DLC film on the supporting layer rather than the diffusion layer (Prihandana et al., 2013). The supporting layer had larger pores than the ones in the diffusion layer, as shown in Figures 3 and 4; in addition, its lower level of conformal coating characteristic allowed the F-DLC film to be deposited on the wall of the porous membrane, without covering its surface.

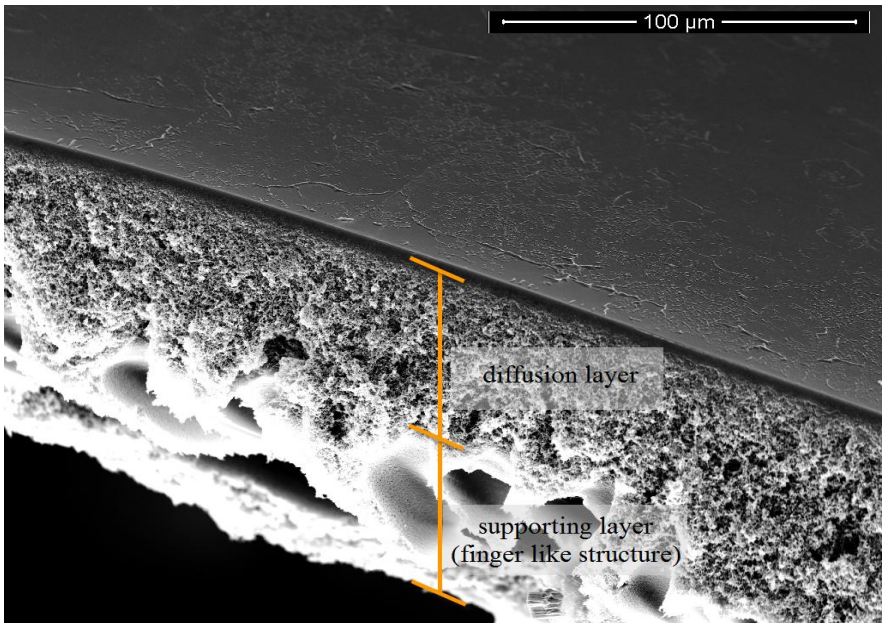

Figure 3 Cross section of PES membrane

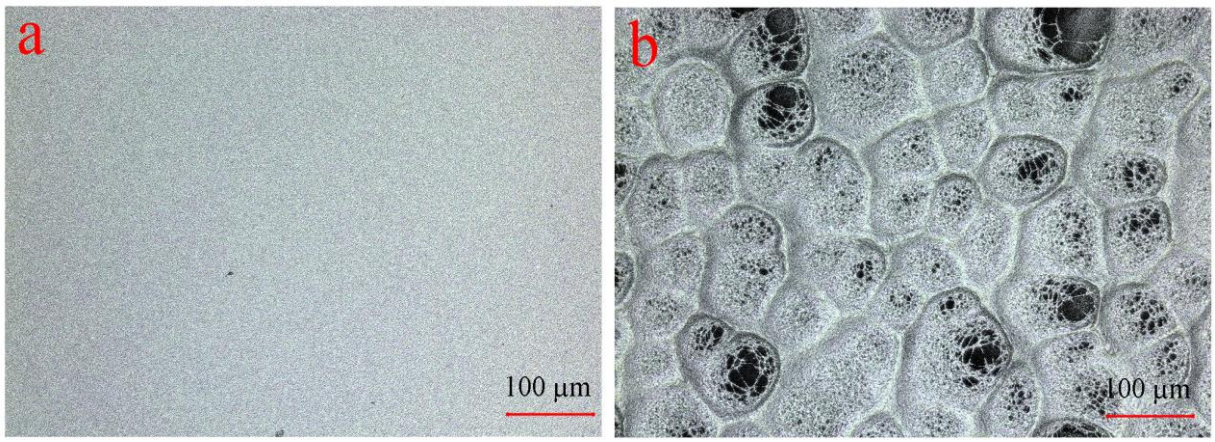

Figure 4 Surface morphology of PES membrane: (a) top surface; (b) bottom surface

In addition, after 27 days of the diffusion test, the parylene film-coated membrane had the highest blood compatibility. As seen in Figure 6, its surface had lower adhesion of blood clots. This confirms that parylene film successfully improved the PES membrane's blood compatibility. As for the membrane coated by F-DLC film, the number of blood clots was almost the same as in the bare PES membrane surface. The explanation behind this result is the poor adhesive strength of F-DLC film onto the membrane surface. During the diffusion test, the blood flow wiped the F-DLC film off the surface, with blood clots appearing as a result.

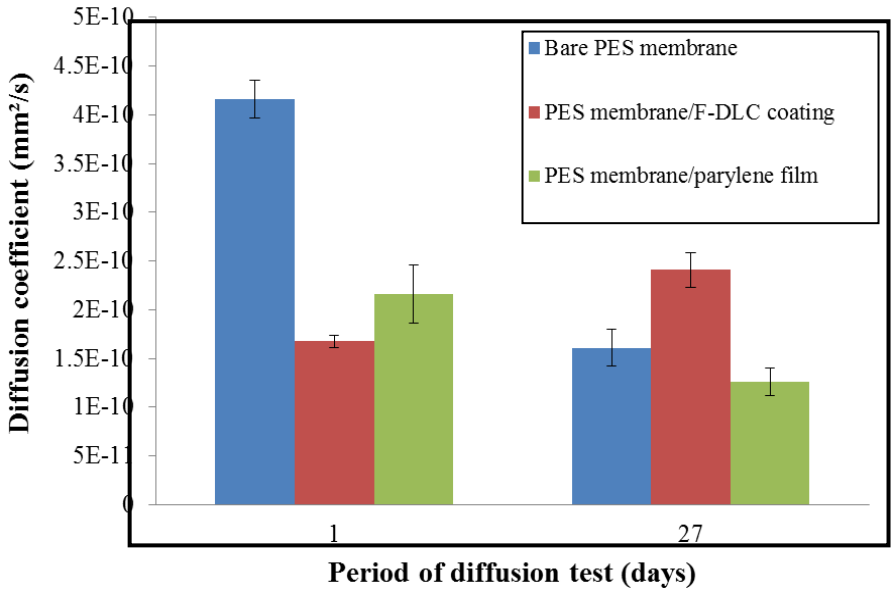

Figure 5 Diffusion coefficients of the membranes

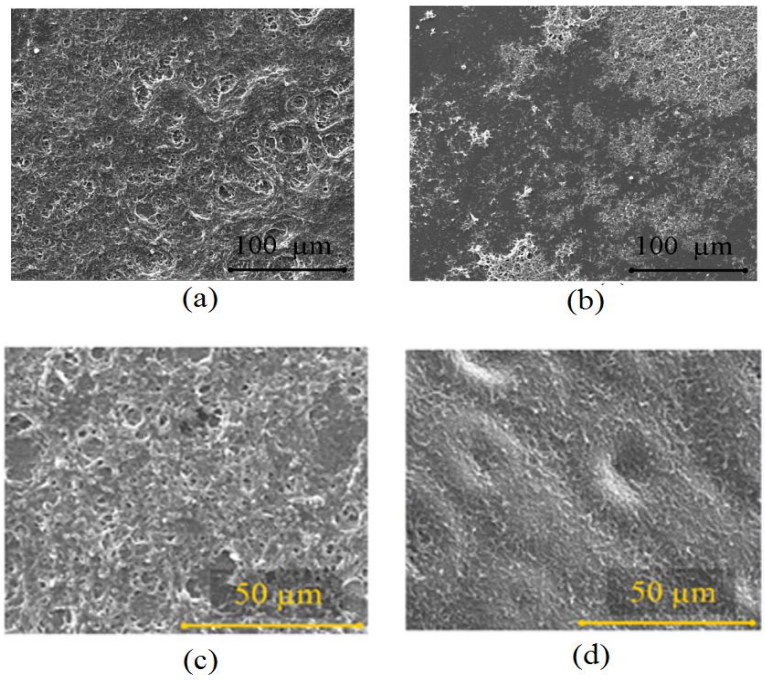

Figure 6 Scanning electron images of the membrane surface after long-term diffusion test: (a) Bare PES membrane (diffusion layer surface); (b) PES (diffusion layer surface)/parylene; (c) Bare PES membrane (supporting layer surface); (d) PES (supporting layer surface)/F-DLC (Prihandana et al., 2013)

Based on the studies above, it can be demonstrated that coating materials improve membrane blood compatibility in different ways. Parylene film has a superb conformal coating characteristic, making it ideal for coating on the diffusion layer of the membrane. Conversely, F-DLC film is a more brittle, harder-coating material and has a worse conformal coating characteristic than parylene film, making it more suitable for applying on the microporous side, which is the supporting layer.

4. CONCLUSION

This study reviewed the application of parylene and F-DLC film to improve the PES membrane's blood compatibility. Based on the results, parylene film provides greater protection on the diffusion layer of the membrane, While F-DLC film improves blood compatibility of the membrane's structural layer. In conclusion, both membranes improve the performance of the PES membrane in different ways.

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