Evaluation on the UV-Shielding Performance of Self-polymerized Dopamine-blended Membrane

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Abstract. Herein we reported the UV resistance evaluation of PVDF membrane which modified through a new blending combined polymerization method. The membrane was prepared by means of non-solvent induced phase separation process in which dopamine was blended altogether with polyvinylidene fluoride polymer in a dimethylacetamide solvent. The blended membrane was further modified by immersion into tris-HCl system to trigger the self-polymerization of dopamine into polydopamine. The UV stability performance was studied by exposing the membrane to the UV light for 5 days. The morphological change of the membrane was observed by using scanning electron microscopy analysis. The results revealed that, with only blending the dopamine into the membrane system, the membrane was severely damaged after UV exposure. However, by simply immersing the blended membrane into buffer Tris-HCl solution, the membrane showed minimal morphological damage after similar UV exposure treatment. This membrane can be a promising choice for the photocatalytic membrane reactor application.

1. Introduction

Recently, it has been reported that polydopamine (PDA) has the ability to scavenge UV-induced free radicals and protects materials against photodegradation [1-3]. The ability of PDA in shielding materials from UV radiation is due to its catechol chain components consisting of very long OH and NH groups [4]. These groups are electron donors and are able to deactivate UV-induced free radicals through electron donor reactions [3]. Modification of PDA for this purpose has been applied in several fields of research such as fabrication of fiber [5], clay materials [6], membrane [1, 2], etc. In membrane technology itself, the application of this research is very useful for photocatalytic membrane reactor application because direct and continuous exposure of the membrane to UV light will morphologically damage the membrane and affect on mechanical properties and overall performance [7].

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The ability of PDA as a UV-protector for photocatalytic membrane has been previously reported by Feng et al [1] and Wu et al [2]. Feng and team [1] used a coating modification method in which the PDA layer formed directly on the membrane surface. Their modified PSf/PDA/TiO$_2$ membrane revealed to have an excellence UV resistance and self-cleaning property. However, the presence of the PDA layer blocked the membrane surface pores thereby declining the permeation performance. On the other hand, Wu et al [2] continued the modification with a similar goal but through blending technique. They prepared PDA and TiO$_2$ into nanohybrid particles then blended in casting solutions. This process produced a membrane with desirable pore properties resulting in high flux production. However, because TiO$_2$ as a photocatalyst particle was blended in the membrane, the photocatalysis reaction does not take place effectively hence the self-cleaning performance was slightly low.

In this study, we report a new method of dopamine-based modification to produce membranes with good UV-shielding performance without abandoning their permeation and antifouling properties. The membrane is prepared by triggering the polymerization of polydopamine from a dopamine-blended polyvinylidene fluoride (PVDF) membrane. We have previously reported in detail the permeate and antifouling performances of this membrane [8], hence, for this reason in this paper we will continue the study by only reporting its UV resistance evaluation. This membrane has the potential to be used for the membrane photocatalytic reactor as there is a thin PDA layer growing on the membrane surface from the polymerization of dopamine which has been blended in the membrane system. The presence of PDA layer can be used as a medium for attaching photocatalysts and also as a free radical scavenger. The evaluation of membrane UV resistance performance is evaluated by observing the morphological changes after 5 days of exposure to UV light.

2. Experimental

2.1. Materials, Polymer PVDF (Solef 6020, Solvay Polymer, USA), and Dimethylacetamide (DMAC, Wako Pure Chemicals, Japan) were the basic materials used for membrane preparation. As an additive, dopamine hydrochloride (DA) which purchased from Sigma Aldrich (Germany) was used. Tris-HCl (Wako Pure Chemical Industries, Japan) with a pH of 8.8 was employed as a base buffer to trigger dopamine polymerization. DI water was used as a non-solvent during membrane preparation and for other solvent necessities.

2.2. Preparation and Modification, The membrane preparation procedure was carried out exactly as we reported in the previous study [8]. Membrane casting solution consisting of PVDF, DA, and DMAC with a respective mass of 15, 2, and 85 grams were dissolved altogether until homogeneous and then prepared using the non-solvent induced phase separation method. The blended dopamine membrane was immersed in a Tris-HCl solution with a pH of 8.8 for 24 hours.

2.3 UV Radiation experiment, This experiment was carried out by adapting that reported in our another work [7]. UV lamp (SUV-16, AS ONE, Japan) with a power of 22 W and a wavelength of 254nm was used as a source of radiation. The experiment was carried out in a closed condition with the sample-to-lamp distance of 5cm. The exposure and observation were conducted for 5 days.

2.4 Membrane Characterization, Field-Emission Scanning Electron Microscopy (FE-SEM, JSF-7500F, Jeol Co. Ltd., Japan) was used to observe changes in membrane morphology before and after UV exposure. Before analysis, the membrane was freeze-dried overnight then coated with an osmium coating. The data recorded was only surface morphology at magnification 1000x.

3. Results and Discussion

To see whether the PVDF membrane modified by PDA through polymerization techniques after blending succeeded in protecting the membrane from UV exposure, an evaluation was carried out by
observing the changes in morphological structure. Morphological changes after the membrane was exposed to UV light were analyzed using SEM instrument. The results of the analysis are shown in Fig. 1. From Fig. 1 it can be seen that the dopamine-blended membrane (P-D0) has a porous surface which supported by the porosity evaluation results reported previously [8]. After being exposed for 5 days to UV light, the P-D0 UV-5 membrane has a much more porous surface. The surface pore is seen to have a sponge-like shape which is due to the damaging effect of photodegradation [9]. The visible dust-like piles on the membrane surface are presumed to be degraded membrane layers. This kind of morphological condition will negatively impact on the membrane separation performance. As for the P-D24 UV-5 membrane, the damage experienced after UV exposure is almost identical to that of the P-D0 UV-5 membrane, which is in form of pore enlargement on the membrane, however, the damage is not as severe. This is because initially (before UV exposure) the P-D24 membrane has a less porous surface due to the presence of a PDA layer formed through tris-triggered polymerization [7].

![SEM photographs of P-D0 and P-D24 membranes before and after 5 days exposure to UV](image)

**Figure 1.** The SEM photographs of P-D0 and P-D24 membranes before and after 5 days exposure to UV

From the result, it can be concluded that the existence of the PDA layer is succeeded in protecting the membrane from photodegradation. Though, when compared with the results of experiments reported in our previous work [7] using the common coating method, the results are not as outstanding. This is because, with the usual coating process in dopamine + Tris-HCl solution, the PDA layer formed is thicker than this method. However, because the PDA layer is not too thick this method can produce membranes with good permease performance and decent selectivity as well.

The UV resistance ability of the polymerized dopamine-blended membrane (P-D24) comes from the presence of catechol groups from PDA which function as a radical scavenger. After modification, the presence of these groups consisting of NH and OH can be observed from the results of the IR analysis shown in Fig. 2 [8]. These groups minimize the occurrence of photodegradation by binding to radical compounds with H atoms through the electron donor reaction [3, 7].
4. Conclusions
Herein we reported the UV resistance evaluation of PVDF membrane which modified through a new blending combined polymerization method. The UV stability performance was studied from the membrane morphological change after exposure to UV light for 5 days. The results confirmed that, with only blending the dopamine into the membrane system, the membrane was severely damaged after UV exposure. However, by simply immersing the blended membrane into buffer Tris-HCl solution, the membrane showed minimal morphological damage after similar UV exposure treatment. This membrane can be a promising choice for the photocatalytic membrane reactor application.

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