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Deposition of polydopamine on the surface of Polyvinylidene Fluoride (PVDF) membrane as A UV-Shielding layer

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Abstract. This paper discusses about the influence of polydopamine layer in enhancing UV resistance of PVDF membrane for membrane photocatalytic reactor application. The PVDF membrane was prepared by common NIPS method using DMAc as a solvent and PEG as a pore-forming additive. The polydopamine layer was deposited on the membrane surface by the facile dip-coating method through Tris-buffered dopamine polymerization. The UV-shielding effect of PDA layer was studied by comparing the changes in pure and PDA coated membrane coating before and after UV irradiation. The studied effects are in terms of changes in chemical, morphological structure and mechanical properties which observed by means of ATR-FTIR, FESEM instrumental analysis, and tensile measurement, respectively. The IR analysis showed that after PDA coating, the membrane surface is rich of catecholamine groups which greatly contributed as free radical scavengers. The change in chemical structure was seen on pure membrane which attributed to the rearrangement of polymer chemical structure caused by UV-induced photodegradation. FESEM imaging results showed that with PDA coating the membrane surface showed minimal damage in comparison to that of non-coated PVDF membrane. These results altogether confirmed, that the PDA layer can protect the membrane surface from UV-initiated free radicals attack.

1. Introduction

In general, it is a well-known fact that most of the polymeric materials are sensitive to environmental influences such as temperature, humidity, and light [1-3]. Same case goes to the polymer-based membranes, if it is continuously exposed to light (either UV or visible light), for instances photocatalytic membrane, as the time passes the membrane will be damaged because the quantum energy of UV light is sufficient to break the major polymer chains and disrupt the molecular structure of a polymer [3]. This phenomenon is commonly known as photodegradation. Photodegradation will result in morphological damage to the membrane, as well as a decrease in mechanical strength that culminates in the short lifespan of the membrane [2, 4].

Photodegradation occurs in three major stages: initiation, propagation, and termination. Initiation is a stage that occurs when energy from UV light is absorbed by the membrane which can break down the chemical chains of the polymer and produces free radicals. At the propagation stage, free radicals

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will react with oxygen and produce peroxy radicals. These radicals will steal the H atoms from the polymer chain and react to form new hydrocarbon radicals such as hydroperoxides etc. this will result in the backbone cleavage of O-O bonds which will be followed by the occurrence of bond scission. Termination is when at least two free radicals combine with each other and result in the formation of new components which eventually lead to changes in the morphological structure and mechanical failure [4, 5].

One of the solutions to prevent or at least reduce the occurrence of photodegradation of polymeric membranes is by protecting it using a scavenger material which capable of being a membrane shielding from UV attack. One of such materials is polydopamine (PDA) [6-9]. In addition to being frequently used as a membrane modifier due to its hydrophilic characteristics [10], PDA is also reported to have high resistance to UV. The UV shielding activity of polydopamine is attributed to the rich content of the catecholamine functional groups (OH and NH) which capable of catching the UV-initiated free radicals before they get to attack the membrane [11-13]. In this study, the shielding ability of the PDA layer was studied. The membrane used was Polyvinylidene Fluoride (PVDF), PDA was incorporated on the surface of the membrane by dip-coating technique. The observed effects are in terms of changes in chemical and morphological structure as well as mechanical properties.

2. Experimental

2.1. Materials

The membrane employed in this study was based on PVDF (Solef 6012, Solvay Specialty Polymer, USA), with DMAc as a solvent and PEG 1000 Da as a pore-forming agent. Both of those materials were purchased from Wako Pure Chemical Industries, Japan. Dopamine hydrochloride (Sigma Aldrich, Germany) and Tris (2-amino-2-hydroxymethyl-1,3-propanediol) (Wako Pure Chemical Industries, Japan) were used to prepare dopamine coating solution.

2.2. Preparation and Modification of PES Membrane

The membrane was prepared by following the procedure reported in our previous work [14]. In detail, PVDF, DMAc, and PEG were mixed with the composition ratio of 15:85:10 wt% then stirred with heating at 60°C to form a homogeneous solution. This solution was then cast on a glass plate using a casting knife with a controlled thickness of 2 mm and then dipped in a water-filled coagulation bath until the membrane film was detached from the glass plate. The finished membrane was then dipped in a 15mM dopamine solution (Tris buffer: pH 8.8) with dopamine concentration of 2 g/L for 2 hours. After the dip-coating was completed, the membrane was then rinsed using distilled water and isopropanol alternately to wash the weakly-bonded PDA on the membrane surface.

2.3 UV Radiation experiment

UV exposure to the membrane was performed using a UV-Lamp instrument (22W, SUV-16 254nm, AS ONE, Japan) which placed in a tightly sealed lab-made box. The membrane sheet was placed at a distance of 5 cm below the UV lamp. The experiment was conducted for 5 days, the sample was taken on day 3 and day 5 for characterizations.

2.4 Membrane Characterization

Characterization on surface morphology, chemical composition and mechanical properties of the membrane before and after UV radiation was performed using the Field-Emission Scanning Electron Microscopy (FE-SEM, JSF-7500F, Jeol Co. Ltd., Japan), the Fourier-Transform Infrared Spectroscopy Attenuated Total Reflectance instrument (FTIR-ATR) (Thermo Scientific iD5 ATR- Nicolet iS5 FTIR Spectrophotometer, Japan) and a tensile test instrument (Autograph AGS-J, Shimadzu Co., Japan), respectively. Before analysis, all samples were dried using freeze drier (FD-1000, Eyela, Japan).

3. Results and Discussion

3.1. Membrane Chemical Composition

Using Fourier Transform Infrared Spectroscopy-Attenuated total reflection (FTIR-AR), analysis of the membrane surface chemical structure was performed to confirm the successful deposition of the PDA layer. Figure 1 shows that after coating with the PDA, there is a noticeable change in the chemical composition of the membrane marked by the emergence of the major components of the PDA, i.e., amine and hydroxyl groups [8, 12]. For detail, in the wavenumber range of 1500–1711 cm^{-1} appeared a new peak due to the bending and scissoring vibration of the N-H group, in addition, at wavenumber ranging from 3300 to 3600 cm^{-1} marks the presence of OH and NH groups of catecholamines contained in the PDA [8, 12, 15]. These are the specific groups which cause PDA to have a superhydrophilic and high free radical scavenger traits.

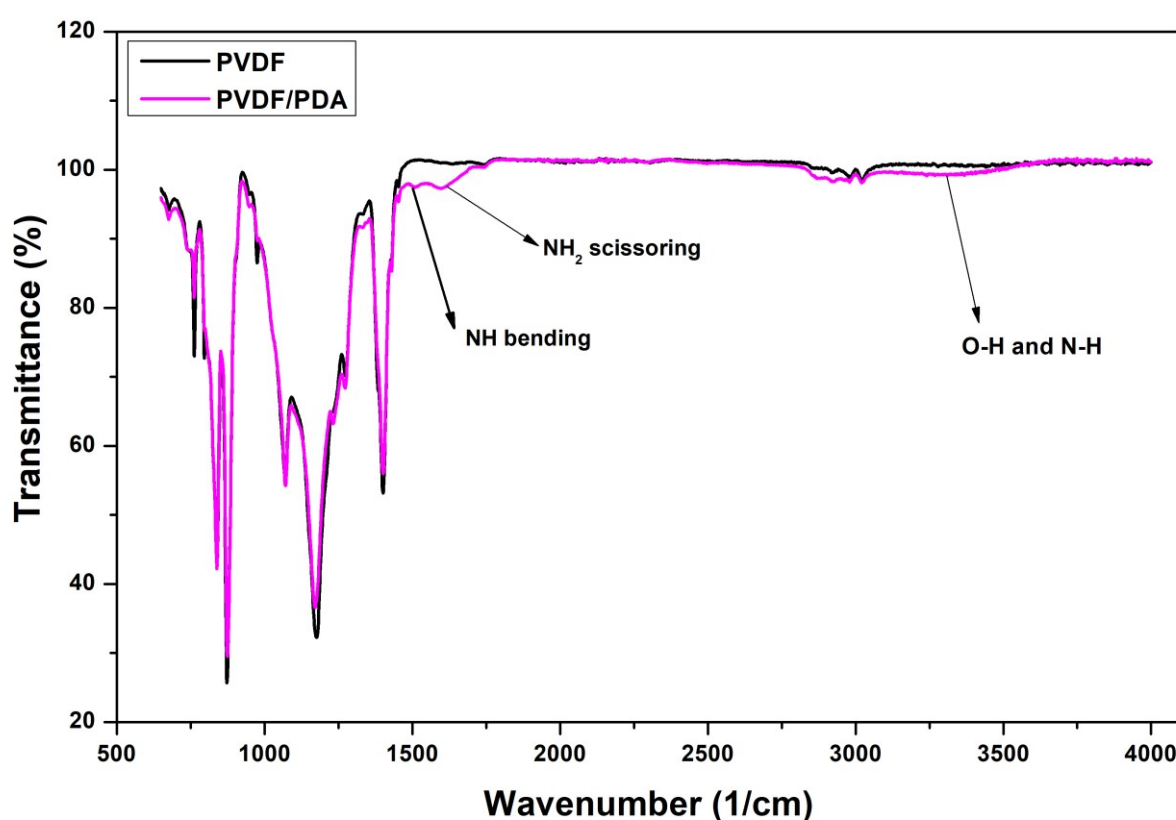


Figure 1. IR Spectra results of PVDF membranes with and without PDA coating

To further confirm the ability of PDA layer as a UV shielding against the membrane, FTIR analysis was also done on the membrane after UV radiation. It is shown in Fig. 2 that, for a pure PVDF membrane, after 5 days of UV exposure, a new peak occurs in a wavenumber 1717 cm^{-1} which denotes a C=O group of ketone [16]. The sudden presence of ketone and aldehyde on an irradiated membrane is attributed to the effects of photodegradation. When UV is irradiated on a polymeric material, it will result in the formation of free radicals which will disrupt the main chemical structure of the polymer, which through several stages of the reaction will produce new compounds, which are generally reported as ketones [5]. As for the PDA coated membrane, there is almost no change in IR spectra results either before or after UV exposure. This is due to the presence of functional groups of catecholamine (OH and NH) of PDA that have high radical scavenging activity which operates by deactivating UV-induced free radicals through the electron donor process [11, 17, 18].

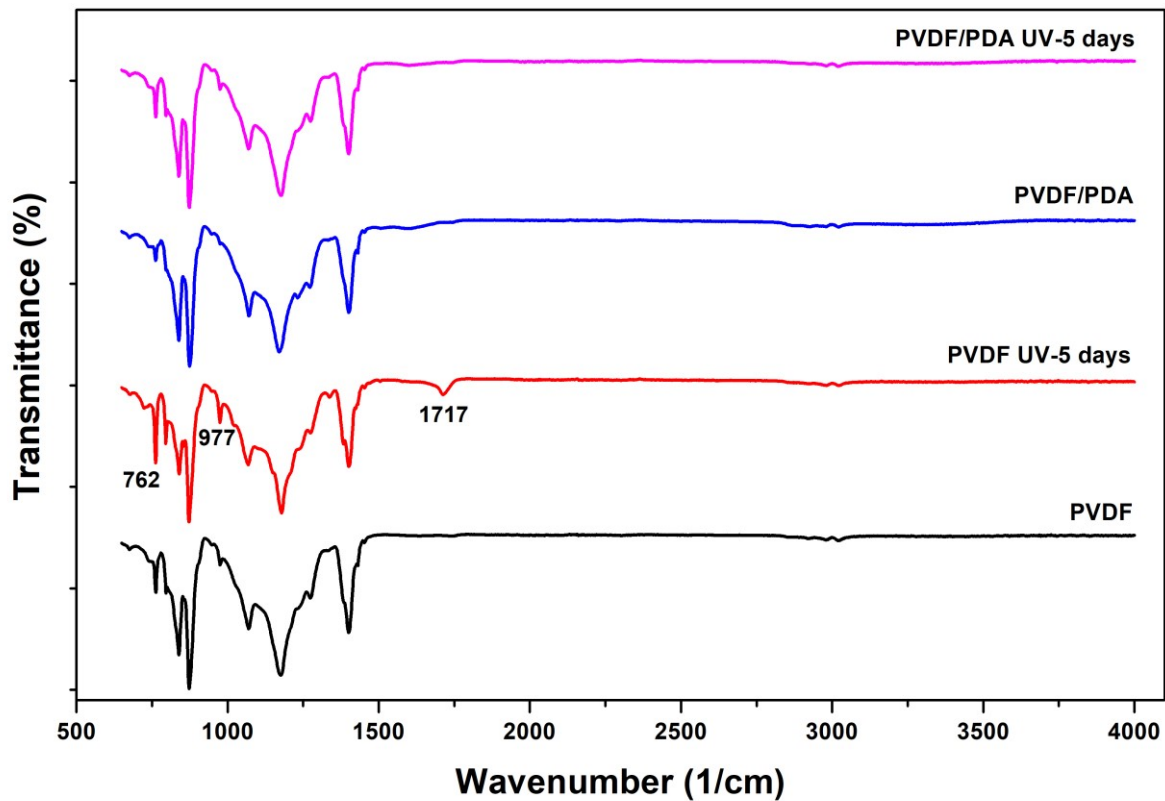


Figure 2. IR Spectra results of PVDF membranes with and without PDA coating before and after UV irradiation

3.2. Morphological Structure

To further explore the effect of PDA coating conditions as UV shielding layer for the membrane, FESEM observation was conducted on pure and PDA coated PVDF membranes of different dopamine concentration and coating time before and after 5 days of UV illumination. From Fig. 3, it is clear that the pure PVDF membrane is severely damaged after UV exposure. Even with the exposure duration of three days only, the deformation that occurs is already significant. Deformation is seen in the form of cracks on the surface also the enlargement of pore size.

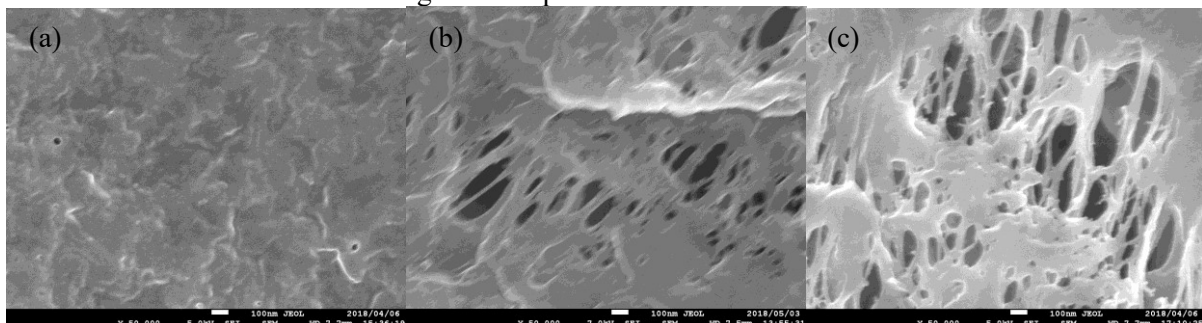


Figure 3. FE-SEM imaging of PVDF membrane (a) before, (b) after 3 days, and (c) 5 days of UV exposure

On the irradiated PDA modified membrane (Fig. 4), a similar type of damage is seen but with way more minimal scale. This once again confirms that the PDA coating is successful in blocking the occurrence of photodegradation of the membrane.

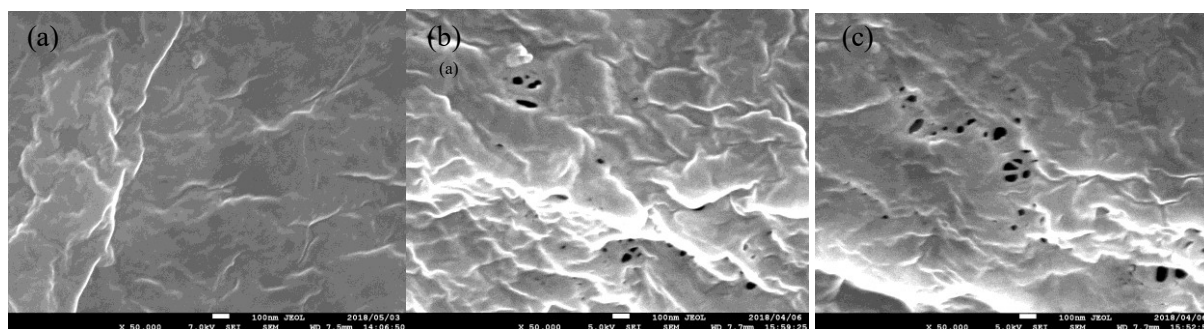


Figure 4. FE-SEM imaging of PDA coated PVDF membrane (a) before, (b) after 3 days, and (c) 5 days of UV exposure

As an additional information, minimal damage is still visible on the membrane coated with PDA presumably because the coating time is still relatively short i.e. only 2 hours. As reported by Zhu and co-workers [19] on their extensive study on characteristics of polydopamine layer on PVDF membrane, in short coating time the polymerization that occurs is not long enough to create a thicker deposited PDA layer on the membrane surface which means free radical scavenger functional groups such as N-H and OH are not sufficient to completely protect the membrane from UV attack. Similar results and reasoning also affirmed by some other relevant literature [20, 21].

3.3. Mechanical Properties

To better explain the effect of PDA coating parameters on UV resistance, mechanical strength data of all the prepared membranes before and after 5 days irradiation are presented in the form of tensile and elongation at break retention as shown in Fig. 5 and 6, respectively. Retention of mechanical properties is obtained by comparing the value of tensile or elongation at break of the sample after UV radiation and that of before UV radiation. As seen from Fig. 5, after only 3 days of irradiation, the tensile at break of original PVDF membrane already decreased significantly by almost 40%. After 5 days of irradiation, the tensile continued to fall dramatically by 60% from its original (before irradiation) tensile value. Meanwhile, for the PDA-coated membrane, the decrease is very minimal even after being exposed to UV for 5 days. This finding is closely correlated with the surface damage caused by UV-induced photodegradation [3] which is greatly supported by the FE-SEM imaging results in Section 3.2. Damage formed on the membrane makes the membrane weakens and breaks easily during tensile testing. In the PDA coated membrane, reduction of tensile is only by 7% on the third day of exposure and almost stable even on the fifth day. This is because the damage formed on modified membrane is not as severe as that of pure PVDF membrane.

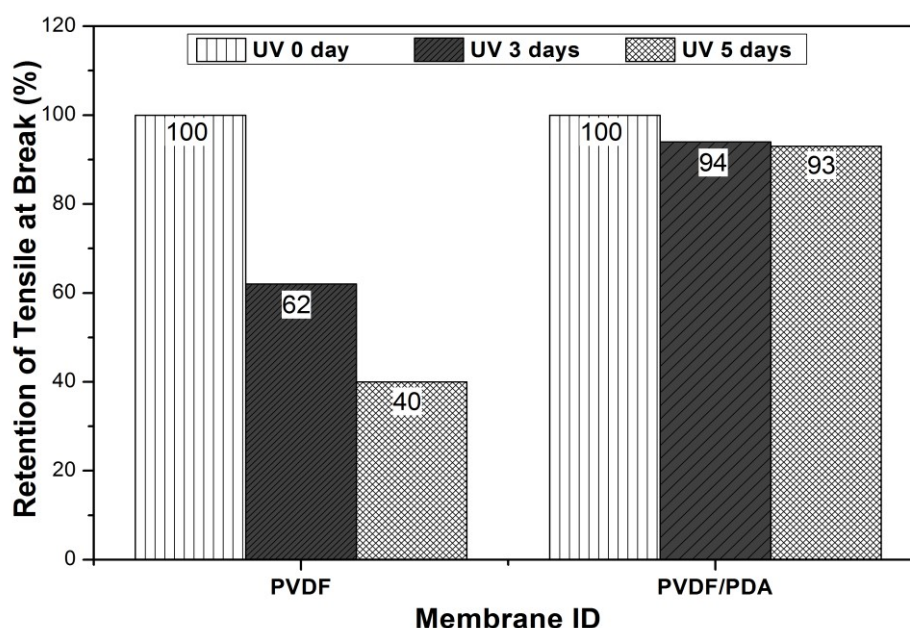


Figure 5. Tensile at break retention of membranes before and after UV exposure

A similar tendency is also observed from elongation at break results. As seen in Figure 6, the ductility of membrane decreased significantly with increasing duration of UV exposure. With only 3 days of exposure, the elongation at break of pure PVDF dropped by 75% (retention value of 25%). As for membrane which shielded by PDA layer, the decline also occurs but not as severe. From the results in Fig. 6, it can be seen that after 5 days exposure membrane is still able to retain about 50% of its ductility. The weakening of the membrane is attributed to the occurrence of embrittlement caused by photodegradation [1, 22].

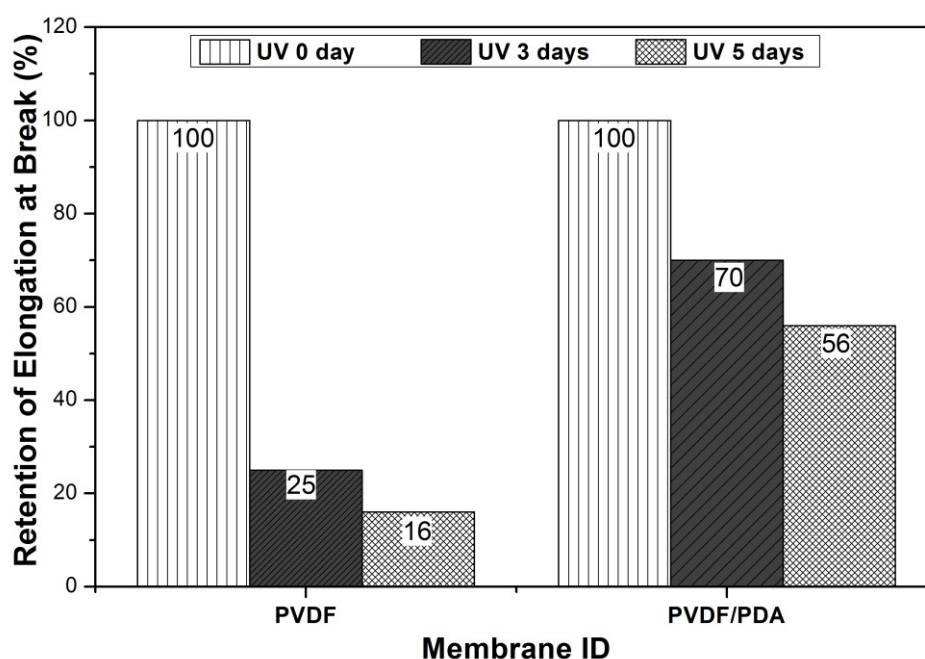


Figure 6. Elongation at break retention of membranes before and after UV exposure

4. Conclusions

Polydopamine layer has been deposited on the surface of the PVDF membrane to improve its resistance to UV radiation. The effectivity of PDA as a membrane UV shielding layer was studied from the membrane changes in terms of chemical composition, morphological structure, and mechanical properties. From the results of the characterization, it was clearly confirmed that PDA layer successfully minimized the effects of UV-induced photodegradation on the membrane.

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6. References

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