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Effects of PEG Molecular Weights on PVDF Membrane for Humic Acid-fed Ultrafiltration Process

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Abstract. This paper reports the performance and characterization of asymmetric PVDF ultrafiltration flat sheet membranes with polyethylene glycol (PEG) of different molecular weight as additives. The membranes were prepared via phase inversion technique by using DMAc as solvent and polyethylene glycol with molecular weights of 2000, 6000 and 20000 Da as additives in the dope formulation. The performance of membrane was characterized using humic acid as natural organic matter source. Membrane properties were evaluated in terms of pure water flux, and humic acid rejection. The results indicated that the pure water flux of membranes increased with the increase of PEG molecular weights. Fourier transform infrared spectroscopy results revealed the presence of PEG in the PVDF/PEG membrane with the significant appearance of the N-CH₃ peak at 2877 cm⁻¹. Scanning electron microscopy analysis was performed to investigate the effects of additives on the morphological structure of the membrane. It was disclosed that the porosity of the resulted membranes increased with the addition of PEG.

1. Introduction

Clean water shortage is a serious problem faced by countries around the world today. Water is abundant on earth, but it is unhealthy to be consumed raw from its sources as it is still contaminated by pollutants, be it natural or waste result from human activities. Natural organic matter (NOM) is a major pollutant commonly found in acidic and low turbidity water sources, particularly those in areas with peat soil. Although the organic compounds contained in the water are relatively harmless, their presence in water should be avoided as those compounds may form carcinogenic byproducts such as trihalomethane [1, 2].

Ultrafiltration is one of membrane technology methods that can be used to eliminate the unwanted contaminants in the water. This separation process is highly favored for its compatibility, ease of use, high organic removal rate and its ability to eliminate the virus in water [3]. Polyvinylidene fluoride (PVDF) has become one of the most attractive organic macromolecule polymers that can be exploited in the fabrication of asymmetric membranes on account of its excellent antioxidation activity, outstanding resistance to chemicals and thermal, high organic selectivity, as well as good mechanical strength and membrane forming [4].

Phase inversion is an important process that is employed in manufacturing an asymmetric porous membrane. The mechanism of phase inversion involves the conversion of a homogeneous polymer



solution of two or more components into a two-phase system which is the polymer-rich solid phase and polymer-poor liquid phase. The solid phase serves in forming the membrane structure, meanwhile, the liquid phase takes a role in forming the membrane pore [5]. Structure and other properties of membranes which prepared by phase inversion depend on many factors. One of those is the presence of additives. Membranes with good rejection and water permeability are usually made by adding suitable additives via specific methods. Plethora kinds of additives have been employed by researchers in order to enhance the membrane properties, for instance, mineral fillers [6], polymers [7, 8], inorganic salts [9], non-solvent and co-solvent [10]. These additives are incorporated into the membranes via various techniques.

PEG is one of the most frequently used polymers as a membrane additive after PVP. Investigation on PEG as an additive has attracted the attention of a great number of researchers due to its simple preparation, as PEG dissolves easily in water and various organic solvents as well as its non-toxicity and low cost. PEG has continuously shown a promising potential in increasing the membrane pore size and permeability. In membrane formation, PEG serves as macro void suppressor and contributes hydrophilic character to the membranes [7]. PEG is also capable in reducing the thermodynamic stability of the polymer dope solution which leads to the formation of a finger-like structure of the membrane [5].

Yunos et al [7] found that the hydrophilic nature of PEG was confirmed by the presence of O-H peak from FTIR analysis result. Hydrophilicity nature of PEG helps to enhance the selectivity and can also play as a pore forming agent. In another study [11], it was proposed that the long-chain hydrophilic molecule in PEG is capable of blocking the protein absorption into the membrane by forming steric repulsion. A group of researchers from China [5] ran a study to investigate the effects of PEG with 6 different molecular weights on the Polysulfone (PSf) membrane. It was disclosed that the pure water flux and hydrophilicity enhanced with the increase of dosage and molecular weights of PEG. However, the mechanical strength of the membrane was decreasing. An extensive study was also conducted by Chakrabarty et al [12] by using PEG with various molecular weights of 400, 6000 and 20000 Da as additives on the Polysulfone membrane with NMP and DMAc as solvents. They concluded that PEG worked as pore forming agent. With the increase of PEG molecular weights, the porosity of the membranes was also rising, which accounted for the rise of PWP and permeability. Idris and Yet [13] reported that the presence of PEG of different molecular weights contributed significantly to the performance of PES membrane. Kim et al [14] carried out an evaluation on the effects of PEG additive of various concentrations and molecular weights over the structural formation and permeation properties of PSf membrane by observing the thermodynamic and kinetic changes of the polymer casting solution. By increasing the molecular weights and ratio of PEG to solvent, the stability of dope solution was found to be dropping, at the same circumstance, the PWP mounted up, however, the solute rejection decreased.

Based on the literature mentioned above, it shows that many pieces of research have been conducted to learn about the effect of PEG molecular weights on the membrane properties and the mechanism of membrane formation. Inspired by previous works, the author intends to conduct a similar study but on a different membrane. In this paper, an attempt is made to investigate the effect of incorporating PEG of various molecular weights on the performance and morphology of the PVDF membrane. The PVDF membranes were prepared via phase inversion technique by using DMAc as solvent and polyethylene glycol with molecular weights of 2000, 6000 and 20000 Da as additives. Effects of molecular weights of PEG on the permeation behavior and morphology of the membranes were discussed. The performance of the membrane was studied by water permeation and humic acid rejection experiments.

2. Methods

2.1. Materials

Polyvinylidene fluoride (PVDF) was used as membrane polymer. N, N-dimethylacetamide (DMAc) as the solvent, Poly Ethylene Glycol (PEG) of different molecular weights (2000, 6000 and 20000 Da) were used as additive, humic acid as NOM sample, and deionized water as non-solvent. Furthermore, casting knife of 2mm and glass plate were employed to cast the membrane and ultrafiltration module.

2.2. Membrane preparation

PVDF of 20 wt % and PEG of 5 wt% concentration was dissolved in 75 wt% DMAc to prepare modified PVDF membranes. The formulation compositions were used for different PEG molecular weights. Pristine membranes without PEG as additive was also prepared to observe the effect of PEG absence on the morphology and performance. The dope solution was blended at temperature of 50°C with vigorous stirring to ensure perfect homogenization. The solution was then carefully cast on the glass plate using casting knife of 2mm space and immersed into the coagulating bath containing DI water as non-solvent at room temperature.

2.3. Morphology test

Morphology test was done by means of Scanning Electron Microscopy (SEM). The membranes were cut into small pieces and then dried by using freeze dryer for 24 hours to let the water content evaporated. Afterward, the membranes were coated with platinum to give the electrical conductivity on the membranes.

2.4. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR (Shimadzu, model IRP Prestige21, serial no. A21004802668LP) was utilized to detect and analyze the polymer functional groups presence in the fabricated membrane. The samples were dried at room temperature in the desiccator for about an hour. The samples were then put on a sample holder. The absorbance data were recorded at wave number range of 400-4000cm⁻¹.

2.5. Pure water permeability (Lp)

The experiment was conducted by passing deionized water through the membrane which beforehand set in the ultrafiltration module. The experiment was done by using trans membrane pressure of 0,5; 1; and 1,5 bar as driving force. The permeate was collected in a flask and its volume was measured every 5 minutes until constant. Pure water flux was then determined by using equation (2.1).

$$J = \left(\frac{\Delta V}{\Delta t} \right) \times A \quad (1)$$

Where J is flux (Lm⁻²hour⁻¹); ΔV is the volume of permeate (L), Δt is time (hour) dan A represents the membrane surface area (m²). The Lp was retrieved from the graphic slope by plotting flux against trans membrane pressure.

2.6. Solute rejection

Humic acid was employed as a natural organic matter (NOM) model. The experiment was carried out by using ultrafiltration experimental set-up with the exact same procedure as that of pure water permeability. The artificial sample was made in a concentration of 10ppm by dissolving dried humic acid (Stigma Aldrich) in deionized water [15]. The sample was flowed through the membrane sheet at trans membrane pressure of 0,5; 1; and 1,5 bar. The permeate was collected in a flask and its volume was recorded at 5 minutes interval time until steady. Flux for each type of membrane and TMP were determined. The concentrations of the humic acid solution and permeate were evaluated by means of UV-VIS Spectrophotometry instrument. The concentrations were used to calculate the percentage of solute rejection with equation as expressed below:

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (2)$$

Where, R is solute rejection (%), Cp and Cf are Concentration of permeate and feed (mg/l), respectively.

3. Results and Discussion

3.1. Membrane morphology

Surface and cross-sectional SEM photographs of PVDF membranes with and without the addition of PEG are shown in Figure 1. The SEM images portray that the PVDF membrane shows a slight change in morphology after the incorporation of PEG. As seen in Figure 1(a) and 1(b), the modified membrane exhibits better distribution, size and number of pores. In the cross-sectional images (Figure 1.c and 1.d), it is shown that the prepared membranes had an asymmetrical structure which composed of sponge-like dense layer and finger-like micro porous support layer [7]. Furthermore, the size of finger-like structure of the PEG modified membrane seemed to be larger than that of in the pure PVDF membrane. This structure contributes a positive effect in improving the permeability of the modified membrane. Hence, it can be concluded that PEG serves as a pore forming agent.

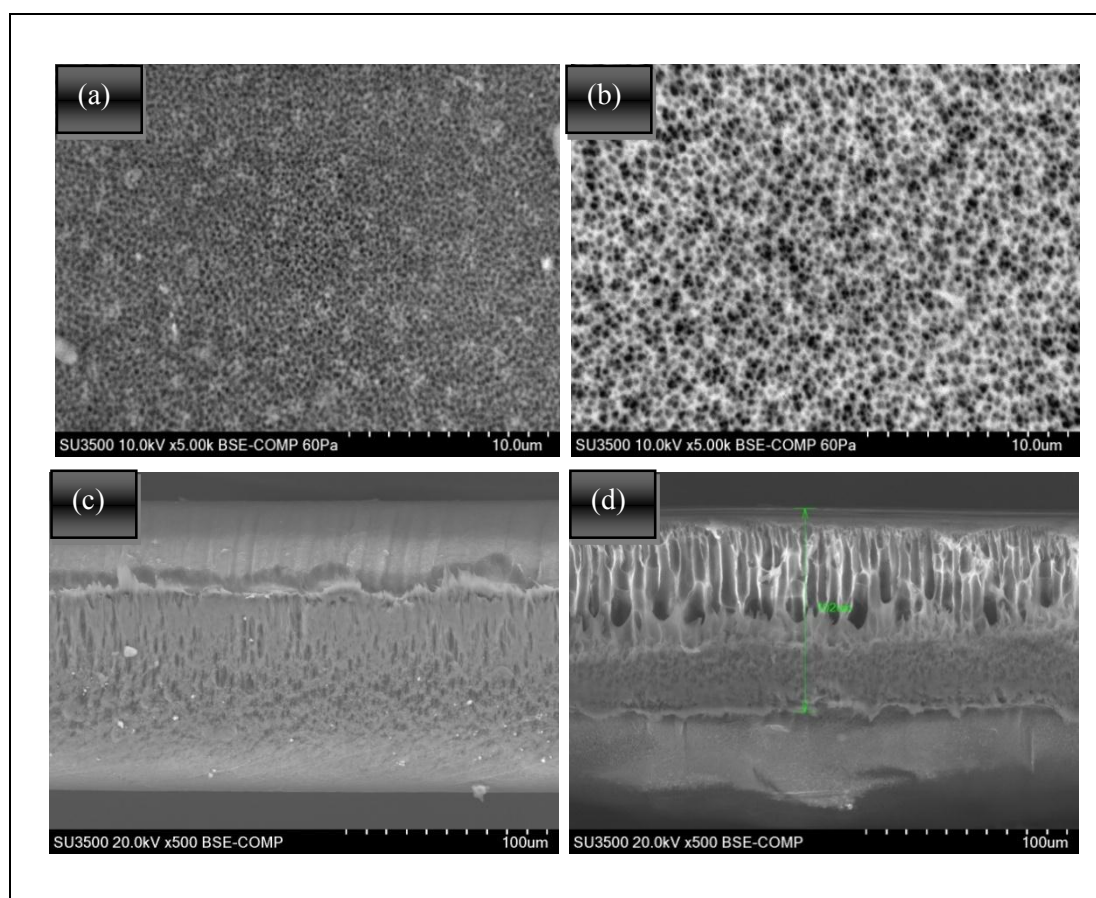


Figure 1. SEM images of PVDF membrane: (a) surface of pure PVDF, (b) surface of PVDF with the addition of PEG 20 kDa, (c) cross-section of pure PVDF, and (d) cross-section of PVDF with the addition of PEG 20 kDa

Wongchitpimon et al [16] proposed an idea regarding how PEG addition and its molecular weights affecting the membrane pores. Bigger molecular weight of PEG means its mobility will be slowing down due to the entanglement of molecular chains, therefore, more of PEG will be trapped in the casting solution during phase inversion. Moreover, if water was used as a non-solvent, it is mostly likely that the entrapped PEG molecules will be dissolved in water (PEG owns a great solubility in water) and be freed from their solid stage which eventually leads to the formation of bigger pore size and macro void.

3.2. Pure water permeability (L_p)

Pure water flux and permeability were obtained from ultrafiltration process using deionized water as feed, the experiment was conducted at trans membrane pressure of 0,5; 1; and 1,5 bar. Flux data for all fabricated membranes as presented in Figure 2. It can be seen that pure water flux went up with increasing of PEG molecular weights. Pure PVDF resulted in a flux of 0 at TMP 0,5 bar, this most likely happened due to the dense porosity of the membrane without additive thus higher pressure is needed as driving force to pass the water through the membrane. On the other hand, PVDF is well-known as a highly hydrophobic polymer with water contact angle above 90° [17], hence water can hardly be adsorbed on its surface. With the addition of PEG, the flux results were successfully enhanced. On the PEG-modified membranes, flux improved up to 60 and 80 $\text{L/m}^2\cdot\text{hour}$ with the addition of PEG 6 kDa and 20 kDa, respectively. This is because PEG works as pore former, the bigger the molecular weight of PEG the bigger the pore of the membrane because the molecular weights of PEG enhance the mean pore size of the membrane [18] therefore the feed solution can easily pass through the membrane.

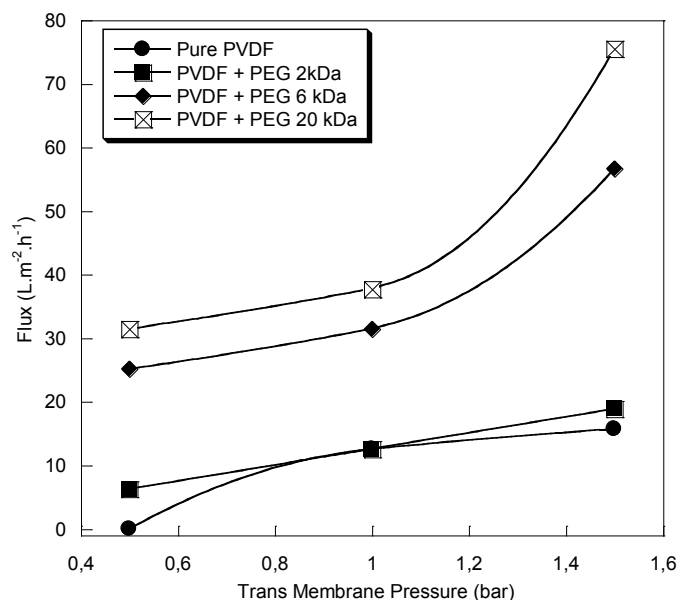


Figure 2. Pure water flux of resulting membranes at various trans membrane pressures

Based on the slope of pure water flux on the trans membrane pressure graphic trend, pure water permeability (L_p) can be obtained. The value of water permeability (L_p) can be used to determine the category of fabricated membranes.

Table 1. Pure water permeability

Membrane	L_p ($\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$)	Types
Pure PVDF	6,293	Nano filtration
PVDF + PEG 2000	7,866	Nano filtration
PVDF + PEG 6000	15,73	Ultrafiltration
PVDF + PEG 20000	22,02	Ultrafiltration

According to Pratomo [19], a membrane with L_p in the range of 10-50 $\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$ lies in the class of ultrafiltration. From the obtained results, it was confirmed that only membranes modified by PEG 6 kDa

and 20 kDa were in the category of ultrafiltration with L_p of 15,73 and 22,02 $L/m^2.h.bar$, respectively. The unmodified PVDF membrane and that with addition of PEG 2000 resulted in an L_p of 6,293 and 7,866 $L/m^2.h.bar$ and belonged to Nano filtration type. Detailed data as provided in Table 1.

3.3. Solute rejection

The effects of PEG molecular weights on flux and solute rejection of PVDF membrane clearly shown in figure 3 and 4, respectively. It was observed that with increasing PEG molecular weights the solute rejection decreased, meanwhile, the flux rose up. Without the presence of the additive, pure PVDF membrane resulted in a rejection of 86,01 % and flux as much as 6,92 $L/m^2.hour$ at 1,5 bar TMP. However, the fluxes for experiment at 0,5 and 1 bar were 0 $L/m^2.hour$. This is because, as confirmed in the SEM images, the neat PVDF had a really small pore size for the humic acid particle to pass over thus a greater driving force was needed. On the membrane modified with PEG 2 kDa, the rejection at ultrafiltration experiment using TMP of 1,5 bar was lowered to 62,56% meanwhile its flux went up to 25,17 $L/m^2.hour$. When the membranes were modified with PEG 6 kDa and 20 kDa the flux kept on increasing up to 31,46 and 69,22 $L/m^2.hour$ meanwhile the rejection percentage plummeted down to 61,40 and 61,35%, respectively. These results indicate that PEG plays a role as a pore-forming agent.

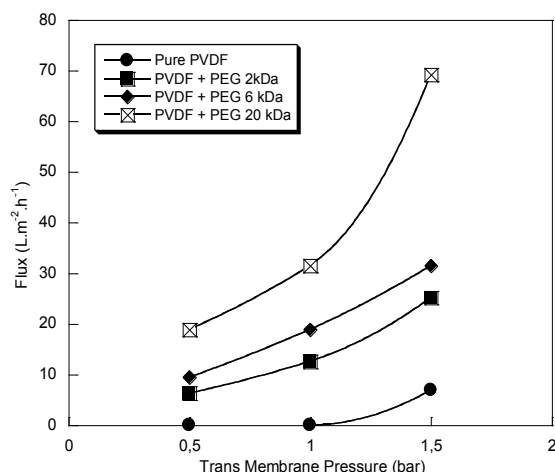


Figure 3. Humic acid flux from ultrafiltration experiment using different membranes at various trans membrane pressure

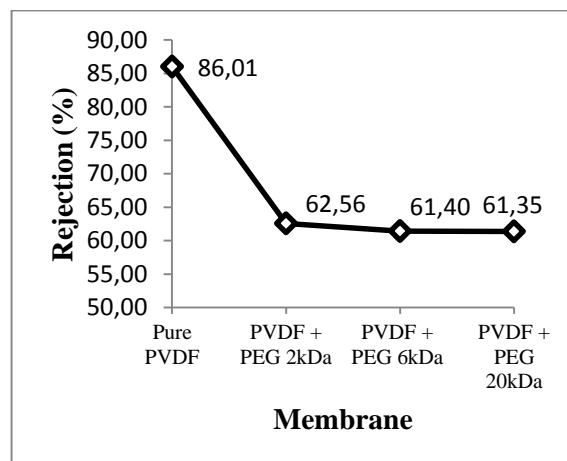


Figure 4. Humic acid rejection of various membranes from ultrafiltration experiment at trans membrane pressure of 1,5 bar

With increasing PEG molecular weights the membrane pore size becomes larger and leads to the formation of macro void thus the greater amount of solute particles can pass through the membrane easily [20], as depicted in the SEM analysis results. In the case of unmodified PVDF membrane, its tight and small pore size causing only less than 20% of the humic acid particle can pass over and the remaining 80% restrained on the membrane surface. In the water purification industry, high rejection is greatly favored as that means high purity of permeate. On the other hand, the great flux is also highly desired in terms of process efficiency.

3.4. Fourier transform infrared spectroscopy (FTIR) analysis

Figure 5 depicts the FTIR spectra of the PVDF membranes with and without the presence of PEG. The main particular structure of PVDF is represented by peaks which located at the wavenumber of 2976,15 and 3020,53 cm^{-1} which indicate the symmetric and asymmetric vibration of the CH_2 group [20]. The PEG addition in PVDF membrane was indicated by the new appearance of a peak at 2877 cm^{-1} which specifies the stretching vibration of aliphatic $-CH_3$ functional group from PEG [7]. This confirmed that PEG was successfully incorporated in the membrane. The intensity of CH_2 in PVDF weakened after

the addition of PEG, from the absorbance of >3 to $<1,5$ a.u. This phenomenon caused by the occurrence of dehydrofluorination [21].

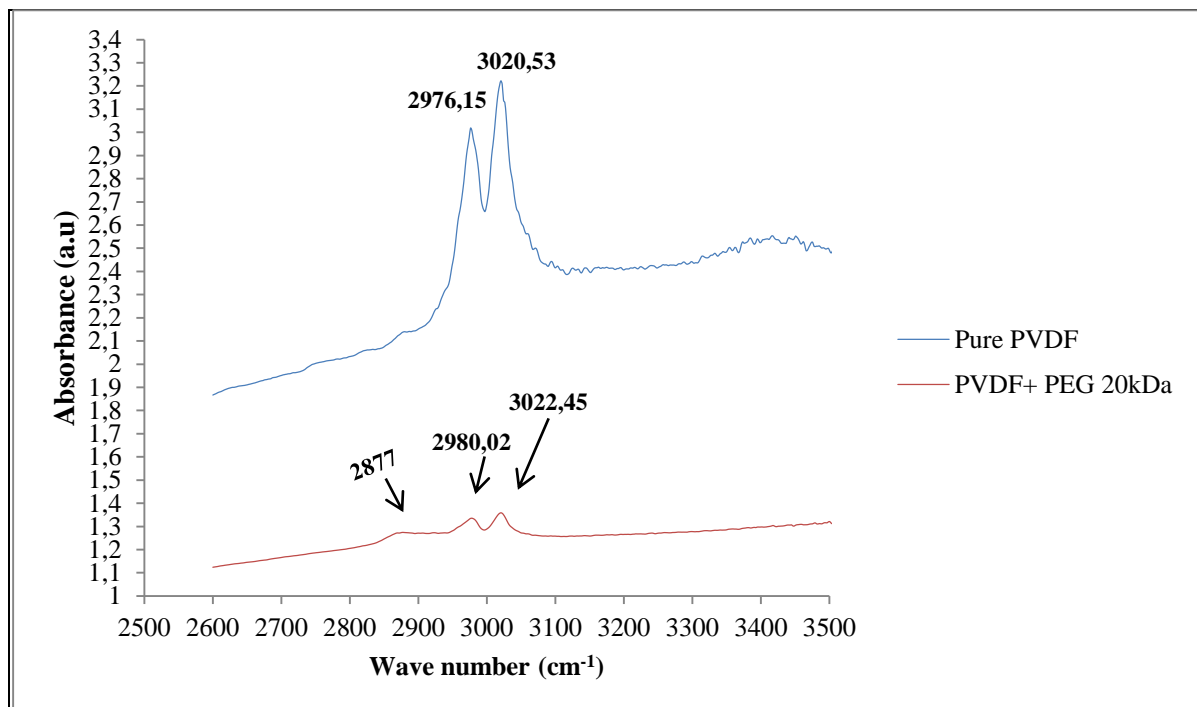


Figure 5. Spectra analysis of PVDF membranes with and without the addition of PEG

4. Conclusion

The effects of PEG of different molecular weights to the PVDF flat sheet membrane in terms of morphology, flux, rejection and chemical composition were investigated. It was revealed that PEG successfully enhanced pore formation of the membrane. As the molecular weight increased, the pure water flux and permeability were also improving. The same effect was also noticed on the flux of humic acid sample, however, with the increasing of flux, the solute rejection plummeted down. Pure PVDF showcased the worst permeability as well as the best selectivity, with resulting humic acid rejection of 80%. FTIR analysis confirmed the modification of PEG into PVDF membrane was successfully done with the appearance of the new peak of N-CH₃ at a wavenumber of 2877 cm⁻¹.

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