Effect of Variation of CE on Surface Morphology and Roughness of PVC-PS-CE Film

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ABSTRACT.
Material selection, material mixing, and material processing to create a thin film affect the surface properties of the resulting layer. The surface properties in question are morphology and roughness. The surface roughness of a thin layer can be used as an indicator that expresses the surface area of a surface. The surface area and roughness of a thin layer applied to a biosensor can affect the sensitivity of the sensor when interacting with an analyte. Thin films that have a large surface area tend to be able to adsorb certain molecules from an analyte. This study showed that the addition of 18-Crown-6 ether (CE) to the polymer membrane consisting of a mixture of Polyvinyl Chloride (PVC) and Polystyrene (PS) caused changes in the morphology and roughness of the membrane. The addition of CE into the PVC-PS-CE membrane causes the size of the cavity on the surface of the membrane to be smaller. The more CE composition in the PVC-PS-CE layer, the more hollow surface morphology. The more CE content, the more cavities on the membrane surface. Based on the resulting morphological analysis, it can be concluded that the addition of CE into the PVC-PS-CE membrane can increase the surface property of the PVC-PS-CE membrane, which is proven by the value of the surface roughness of the membrane. The surface roughness of the membrane increased along with the addition of CE content in the PVC-PS-CE layer, which was indicated by the increasing value of Ra resulting from measurements using the Topography Measurement System (TMS).

Keywords: *Morphology, Crown Ether, Polyvinyl Chloride, Polystyrene*

1. INTRODUCTION

Thin film is a technology that is widely used in various fields, one of which is in the field of sensors. Thin layer technology offers many advantages over conventional sensors, which still use bulk as their functional material. A thin layer of PVC-CE is one of the materials that can be used as a functional sensor material[1]–[8]. In sensor applications, the membrane structure plays an important role because it can affect the sensitivity of the membrane when interacting with an analyte. One example of a structure that plays a role in increasing membrane sensitivity is the surface area[9], [10]. Functional membranes with a large surface area will tend to be able to hold molecules on the membrane surface or even pass molecules into the membrane. With these considerations, PVC-CE membrane can be used as a candidate that has a large surface area.

PVC-CE polymer membrane is a membrane that belongs to the hydrogel group. Hydrogels have a porous structure with sizes ranging from 100-250 nm[11]. The reason for using PVC as a polymer matrix material is because it is affordable (low cost), durable, and has a porous microstructure[12], [13]. The pores in PVC are distributed over the entire surface of the membrane. This indicates that the surface area of the hydrogel layer is relatively large compared to other polymers, so it is effective in increasing the rate of diffusion when an analyte interacts with the membrane.

In this study, the mass percentage of polystyrene (PS) was fixed, while the concentration ratio of PVC-CE used as a functional coating was 9:0, 9:1, 9:2, 9:3, and 9:4. The surface morphology of the PVC-PS-CE layer was characterized using Scanning Electron Microscopy (SEM). The roughness characterization of the PVC/CE layer was carried out using the Topography Measurement System (TMS).

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2. MATERIALS

The QCM sensor used is a QCM sensor with silver electrodes and a resonant frequency of 10 MHz. Polyvinyl Chloride (PVC) used is PVC with a molecular weight of 43,000 g/mol purchased from Sigma Aldrich. Meanwhile,the Crown Ether (CE) used was CE type 18-crown-6-ether with a molecular weight of 264.32 gr/mol which was purchased from the same company. The polystyrene (PS) used is PS with a molecular weight of 192 kDa. The solvent used was Tetrahydrofuran (THF). The composition of PVC: CE is varied from 9:0, 9:1, 9:2, 9:3, and 9:4. The mass percentage of polystyrene used in the PVC/CE mixture was fixed at 18%.

2.1. Preparation of thin film PVC-PS-CE

PVC-PS-CE is made by mixing PVC, PS, with CE into THF solvent. the concentration of the mixture is 4%. PVC-PS-CE was coated on the surface of the QCM sensor using a spin coating technique with a rotating speed of 3000 rpm for 60s. The mass of PS was kept constant (0.072 g), while the composition of PVC-CE was varied 9:0, 9:1, 9:2, 9:3, and 9:4. The QCM sensor which has been coated with PVC-PS-CE, is left for 24 hours at room temperature, so that the THF solvent evaporates.

2.2. Characterization of Surface Property using SEM and TMS

The surface property of the PVC-PS-CE layer was observed using the Scanning Electron Microscopy (SEM) and Topography Measurement System Polytech TMS 1,200. Characterization were made to observed the surface property (morphology and surface roughness) of the PVC-PS-CE film. Surface property image of the PVC-PS-CE film was taken.

3. RESULT AND DISCUSSION

PVC-PS-CE membrane is a membrane that can be used for the detection of heavy metal ions, such as potassium ions. In the PVC-PS-CE mixture, PVC acts as the membrane matrix, PS as stabilizer, while CE acts as the selective compound. CE is categorized as a supramolecule with a cavity composed of a repeating –CH2-CH2O- chain. The selective complex properties shown by CE to metal ions, cause the functionalization of CE into the polymer matrix to increase the selectivity of the polymer membrane. In general, CEs have oxygen, nitrogen, or sulfur donor atoms, which when combined with the cavity diameter allow for the selective complexation of various metal ions. In sensor applications, the structure of the membrane (surface area) can affect the sensitivity of the membrane when interacting with an analyte. This membrane takes advantage of the surface properties to perform its function as a functional layer of the sensor. Roughness is a surface property that can increase the sensitivity of the sensor when interacting with an analyte. Variations in the content of CE compounds in the PVC-PS-CE membrane can affect the surface properties of the PVC-PS-CE membrane. This can be proven by the Ra value of the measurement using TMS (Table 1).

TABLE 1. Roughness value of TMS measurement results

Composition of PVC:CE	Roughness(nm)
9:0	295.9±1.099
9:1	303.0±3.772
9:2	318.6±0.5551
9:3	331.8±1.594
9:4	376.7±0.4026

Based on the data in table 1, we can see that the value of Ra increases with increasing CE content in the PVC-PS-CE membrane. The increase in Ra value on the PVC-PS-CE membrane was significant.

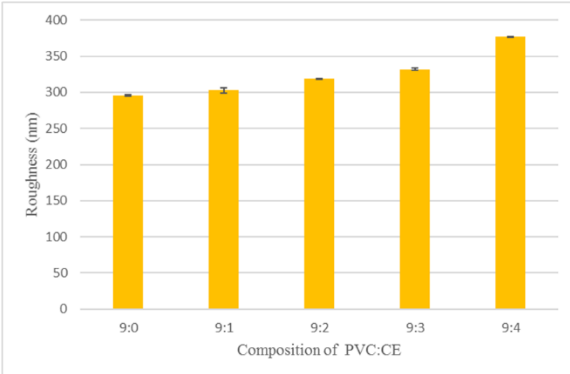
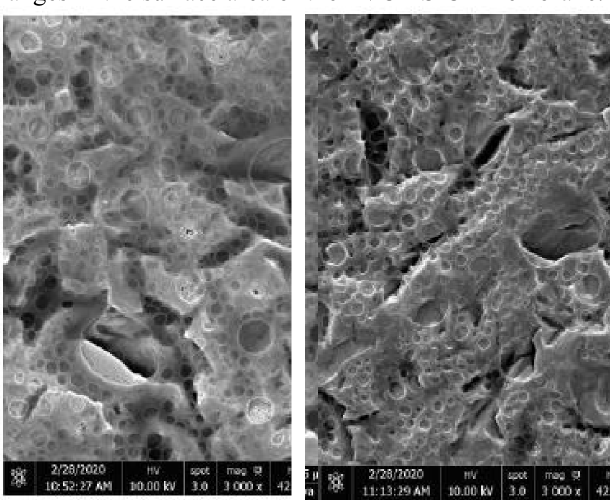


FIGURE 1. The results of measuring surface roughness (Ra) of PVC-PS-CE membrane using TMS: (a) 9:0, (b) 9:1, (c) 9:2, (d) 9:3, (e) 9:4

A change in the Ra value indicates that there is a change in the surface property of the PVC-PS-CE membrane. The more CE content added to the PVC-PS-CE membrane, the Ra value of the PVC-PS-CE membrane increased. The increase in Ra value cannot be used to state that the addition of CE in the PVC-PS-CE membrane affects the surface area of the membrane. Supporting data is needed to ensure that the addition of CE in the PVC-PS-CE membrane causes changes in the surface area of the PVC-PS-CE membrane.



(a) (b)

FIGURE 2. The results of the morphology measurement of the coating PVC-PS-CE using SEM: (a) 9:0, (b) 9:4

Based on Figures 1 and 2, it can be analyzed as follows. In membranes without CE content (9:0 composition), the Cl atoms are randomly oriented along the polymer chain. The Cl atom is also able to leave the chain and bond with other atoms randomly because of its relatively large electronegativity compared to C and H atoms. Due to the relatively large size and electronegativity of the Cl atom, it is difficult for the chains to be close together so the crystallinity area tends to be narrow[14]. So that the surface morphology of the membrane tends to be hollow. When a CE compound is added to a PVC membrane (9:4), which contains O atoms, the Cl atom will not be able to be oriented randomly because the electronegativity of the O atom is greater than that of the C atom. The electronegativity of the O atom: is 3.44 while the Cl atom: is 3.16. In addition, the presence of these O atoms causes the elements contained in the membrane to become denser so that the chains tend to be close together. Therefore, the size of the voids in the 9:4 composition membrane is dominated by small cavities which are evenly distributed and the size of these small cavities is also smaller when compared to the small cavities in the 9:0 composition membrane. This smaller cavity size can increase the roughness and surface area of the PVC-PS-CE coating.

CONCLUSION

This paper shows the effect of adding CE on the surface roughness and surface morphology of PVC-PS-CE membranes. The surface roughness value of the PVC-PS-CE membrane increases with the increase in the CE content in the PVC-PS-CE membrane. The increase in the surface roughness value indicates an increase in the surface area of the PVC-PS-CE membrane, as evidenced by the results of characterization using SEM. The more CE content in the PVC-PS-CE membrane causes the surface morphology of the PVC-PS-CE layer to be more hollow. Based on this analysis, it can be said that the addition of CE to the PVC-PS-CE membrane causes an increase in the surface area of the PVC-PS-CE membrane.

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