Surface Modification of Microfiltration Polypropylene Membrane for Molecular Air Filtration

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Abstract - Microfiltration polypropylene (MPP) membrane has increasingly been used in separation processes due to its good chemical and mechanical stability, high selectivity to submicron particles, and low cost. In this paper, the MPP membrane was modified by coating the surface with a composite polysulfone (PSf)/PEG400/ZnO layer. Then, the modified MPP membrane was used for fine particle removal from air. Performance of modified MPP membrane as a function of polymer and ZnO nanoparticles (ZnO-NPs) concentration in coating solution, and coating time, was investigated. The SEM image showed that the presence of ZnO-NPs in polymer solution generated macrovoids in the coating layer. Permeate flux decreased with increasing polymer and ZnO-NPs concentration, but the flux increased with increasing coating time. Meanwhile, fine particle removal efficiency increased with the increase of operating pressure. A stable air flux of 19 L m-2 h-1 was obtained at ZnO-NPs concentration of 3 wt.%. The removal efficiency of PM1, PM2.5, and PM10 at operating pressure of 2 bar were 70%, 74%, and 70%, respectively.

Keywords: Microfiltration Polypropylene (MPP), coating, ZnO,macrovoids, fine particles, air flux

I. INTRODUCTION

Membrane technology has increasingly been used in air filtration and purification due to its excellent selectivity to airborne particulate matters and aerosols (1, 2). One alternative polymer that can be used for membrane material for air filtration is polypropylene (PP). This polymer provides some advantages, such as excellent mechanical and chemical stability, low cost, and hydrophobic (3-6). Generally, The commercial PP membrane is fabricated by melt spinning and hot/cold stretching, which produced a microporous pore structure (7-9). It has been reported that the microfiltration PP (MPP) membrane was able to remove particles and bacteria with a molecule size of around 0.5 □m (10).

Up to this time, only a few studies were conducted concerning the application of PP membrane for air filtration and purification. Bulejko et al (11) investigated the filtration efficiency of different packing density and pore size distribution of PP hollow fiber membranes when it used to remove particulates with range diameter size from 18 to 100 nm. They found that the filtration efficiency of PP membrane was over 99% for particles above 60 nm dia. Meanwhile, the filtration efficiency for particles size between 36 and 40 nm at permeate velocity of 5 cm/s was 82 - 86%. When the flow rate was increased from 10 to 15 cm/s, the filtration efficiency was decreased to 70 - 84%. In other research, Bulejko (12) used PP hollow fiber membrane with pore size range of 90 - 100 nm to remove submicron synthetic particles (TiO2) from indoor air. The PP membrane removed 99% of particles.

Azis (13) modified the PP membrane by coating the membrane surface with Fe-ZSM-5 solution in ethyl vinyl acetate (EVA) and polyethylvinyl alcohol (PVA) at a constant speed of 2 cm/s. The modified PP membrane was used to remove volatile organic compound (VOC) contaminants in the air, such as benzene, toluene, ethylbenzene, and xylene, at a flow rate of 3.5 cm/s. They found that the efficiency of VOC removal during 1-6 cycles of the filtration process was less than 50%. The removal efficiency was improved when the membrane unit was coupled with UV system. Another particle used in the surface-modified of membrane is zinc oxide (ZnO), which has an antibacterial property and hydrophilic (14). Liang at al. (15) added ZnO nanoparticles with different dosage into polyvinylidene fluoride (PVDF) membrane matrix by multi-cycle filtration technique. The modified membrane showed anti-irreversible fouling property. Leo et al. (16) blended 1 - 4 wt.% of ZnO nanoparticle (21-23 nm) in polysulfone (PSf) solution. The thermal stability of the resulted membrane was improved due to the presence of ZnO in membrane matrix. Furthermore, membrane that coated with ZnO showed good activity against several bacteria, including Bacillus subtilis, Escherichia coli, Staphylococcus aureus, and Staphylococcus epidermidis (17). The antibacterial property minimizes fouling formation on the membrane surface, which extends the membrane lifetime while maintaining the permeate flux (18-21).

In this paper, the PP hollow fiber membrane was modified by coating the membrane surface with composite PSf/PEG400/ZnO solution. The influence of different concentrations of polymer (PSf and PEG400) and ZnO in coating solution on air flux were investigated.

II. METHOD AND MATERIALS

II.1. Materials

Microporous PP membrane was supplied by GDP Filter, with an inside diameter of 200 μm and outside diameter of 400 μm. The type polysulfone (PSf) used in this experiment was UDEL P-3500 MB7, which was supplied by Solvay Advanced Polymer. PEG400 from local supplyer was used as pore performer in the coating layer. DMAc with 99.9% purity is used as a solvent without further purification and supplied by Shanghai Jingsan Jingwei Chemical Co. Ltd. Zinc oxide (ZnO) nanoparticle was obtained from local supplier with a particle diameter of 200 nm.

II.2. Surface Modification of MPP Membrane

The MPP membrane was modified by dip-coating method. The did-coating solution was prepared by blending polymers (polysulfone/PSf and PEG400) in DMAc with the addition of ZnO nanoparticles (ZnO-NPs) as additives. The ratio of PSf:PEG400 in the coating solution was 1:4. The ZnO-NPs were added at various concentration between 1 to 4 wt.% in total weight of polymer solution. The solution was stirred for 12 hours until a homogenous solution was formed. A dip coater equipped with a dipping timer was used to coat the PSf/PEG400/ZnO composite solution on the PP membrane surface. The PP membrane was withdrawn from the polymer solution in constant speed (15 mm/s) and then dried in room temperature for 24 hours until the solvent was evaporated from the membrane layer. The steps of PP membrane coating with PSf/PEG400/ZnO solution was illustrated in Figure 1.

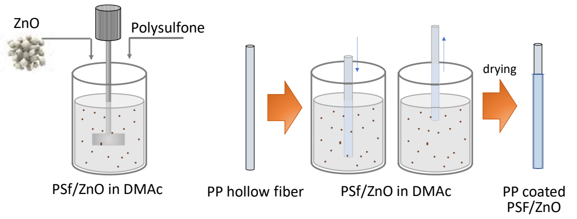


Figure 1. Dip-coating of MPP membrane with PSf/PEG400/ZnO solution

II.3. Characterization of Membrane Morphology by Scanning Electron Microscopy (SEM)

The prepared membrane was characterized by scanning electron microscopy (SEM) to obtain visual information of the cross-sectional morphology of the membrane. The hollow fiber PP membrane sample was fractured cryogenically in liquid nitrogen and deposited with gold using a sputter coater. Then, the sample was probed using a scanning electron microscope (JSM-6510LV low vacuum SEM equipped with a super conical lens).

II.4. Air Filtration Test

The modified MPP membrane, with a total membrane area of 0.005 m2, was bundled in Ushape and potted in a transparent cylindrical module, as shown in Figure 2. The MPP membrane module was connected with a blower to generate dead-end filtration through the membrane. The permeate flow rate was measured by a flow meter. Fine particles (including PM1, PM2.5, and PM10) were measured by a concentration detector near the air outlet of the membrane module at room temperature (25oC) and pressure of 1 bar

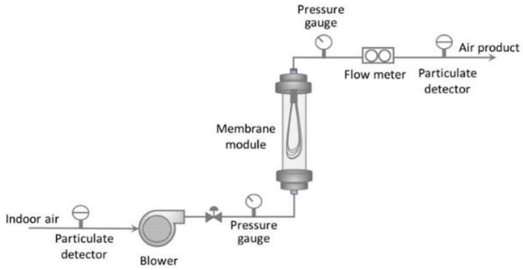


Figure 2. Experimental set up of air filtration

The filtration efficiency was calculated by the following equation:

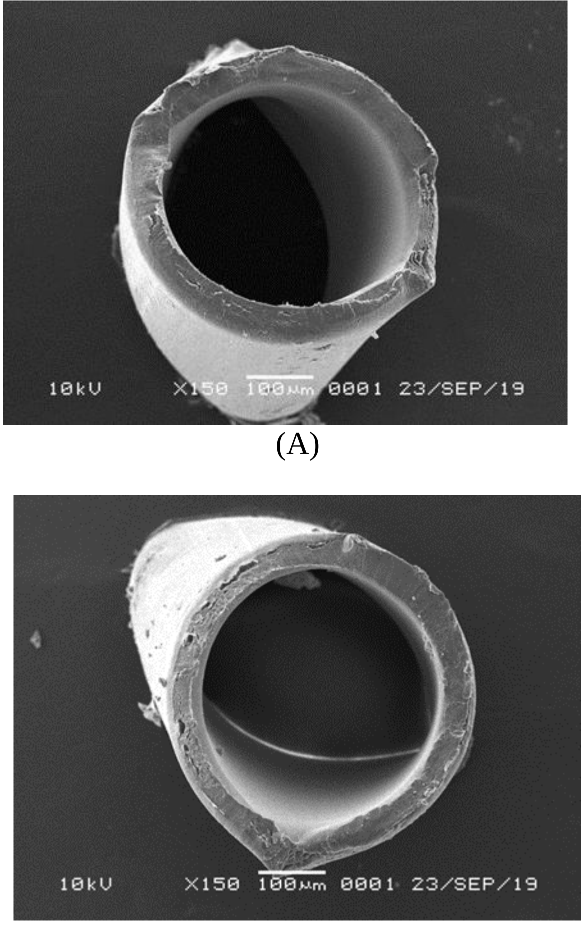
$$\text{Filtration efficiency (\%)} = [1 - C_p/C_f] \times 100\%$$

where Cp is the concentration of particulates at feed and Cf is the concentration at permeate side

III. RESULTS

III.1. The Morphology of Modified MPP Membrane

SEM analysis was utilized to investigate the morphology of modified PP membrane. Figure 3 shows the cross-section SEM image of the coated hollow fiber PP membrane with and without the addition of ZnO particles. Tight membrane layers were formed on both inside and outside of the microporous membrane surfaces, which generated by evaporation phase inversion mechanism. After the PP membrane was withdrawn from the polymer solution, the solvent in the membrane solution was evaporated immediately. The evaporation of solvent led to the solidification of the polymer solution and then formed a tight polymeric membrane structure on the PP membrane surface. A smooth membrane surface was formed when the MPP membrane was coated with coating solution without the addition of ZnO-NPs (Figure 3 A). Conversely, the addition of ZnO-NPs into the coating solution produced irregular structure and clumps of particles. In addition, some voids were found under the coating layer. The immiscibility of the ZnO-NPs and polymers disrupted the PSf chain packing as well as interaction between the PP and PSf membrane, which induced higher voids formation (free volume).



(A)

(B)

Figure 3. SEM of PP Coated PSf/ZnO : (A) without ZnO and (B) with 2% wt of ZnO

III.2. The Influence of Polymer Concentration and Coating Time on Air Flux

Figure 4 shows the influence of polymer concentration on permeate (air) flux of the modified membrane. It shows that the increase of polymer from 6 to 8 wt.% reduces the air flux from 27 to 15 Lm-2h-1. The increase of polymer concentration increased the viscosity of coating solution, which inhibited the growth of membrane pore. Smaller membrane pore size enhanced the intrinsic resistance of the membrane, and consequently, it reduced the permeate flux. The presence of ZnO-NPs in coating membrane solution resulted in lower air flux compared to the absence of ZnO-NPs. It was suggested that the presence of the ZnO-NPs reduced the free volume (or effective pore) in the membrane structure and therefore, the volume of air to diffuse through the membrane was decreased. A slight change in air flux occurred when the ZnO-NPs were added into the solution. The air flux was maintained at 19 Lm-2h-1 when the polymer concentration was increased from 6 to 8 wt.%.

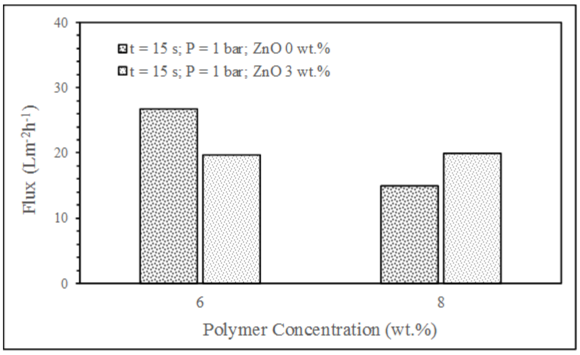


Figure 4. The influence of polymer concentration on air flux at constant operating pressure (1 bar) and dip-coating time (15 s).

The influence of dip-coating time on air flux is shown in Figure 5. The air flux was increased from 21 to 26 Lm-2h-1 or by 23% when the coating time was prolonged from 2 to 15 s. It can be attributed to the decrease of membrane surface roughness with the enhance of dip-coating time. The polymer had sufficient time to arrange the chain before removed from the solution and solidified. In addition, the increase of membrane thickness with the prolongation of dipping time contributed to the increase of solidification time of polymer and allowed the membrane pore to grow. As result, the volume of air through the membrane was enhanced. The same trends were found when the membrane was modified by the addition of ZnO-NPs

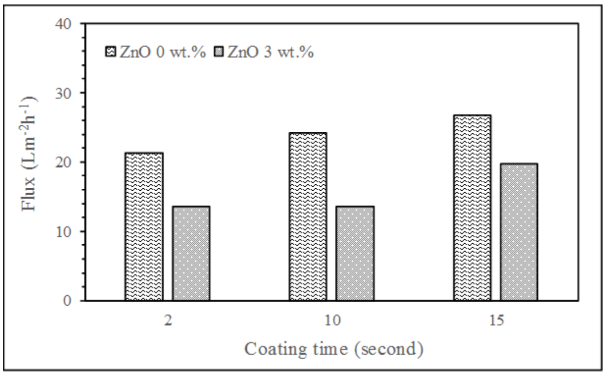


Figure 5. The influence of coating time on air flux at constant operating pressure (1 bar) and polymer concentration (6 wt.%)

III.3. The Influence of Operating Pressure on Permeate Flux

The influence of operating pressure on permeate flux is presented in Figure 6 at a constant dipping time of 15 s and polymer concentration of 6 %wt. When the coating solution was prepared without the addition of ZnO-NPs, the increase of operating pressure from 1 to 2 bar increased the air flux from 26 to 44 Lm-2h-1. The increase of operating pressure enhanced the volume of air through the membrane pore to the permeate side. By adding 3 wt.% of ZnO-NPs into the coating solution, the air flux was decreased by 46% (from 26 to 14 Lm-2h-1). It has been explained that the presence of ZnO reduced the effective pore in the coating layer, which contributed to the decrease of volume of air through the membrane.

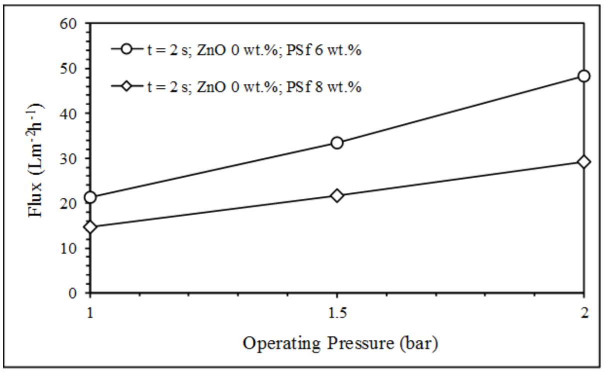


Figure 6. The influence of operating pressure on permeate flux at a constant dipping time (15 s) and polymer concentration (6 wt.%).

III.4. The Influence of the addition of ZnO in Coating Solution on Air Flux

One of the parameters that influences the membrane performance is number ZnO-NPs. In this research, the amount of ZnO-NPs mixed into the coating solution was varied from 0 to 4 wt.% in coating solution. As shown in Figure 7, the air flux was stable until the addition of 2 wt.% of ZnO-NPs. Further addition of ZnO, the air flux begun to decrease. The decrease of voids in membrane structure due to the raise of ZnO-Np concentration in solution reduced the air flux. In addition, the agglomeration of ZnO-NPs occurred when the concentration of nanoparticles was high. ZnO-NPs agglomerate blocked the membrane pore and produced uneven pore distribution along the membrane structure, which contributed to the decrease of air flux.

Figure 8 shows the influence of ZnO concentration on air flux at different polymer concentrations, i.e. 6 and 8 wt.% and constant dip-coating time of 15 s. Both membranes were operated at a constant operating pressure of 1 bar. At polymer concentration of 8 wt.%, a significant change occurred when the ZnO-Np was added up to 2 wt.% in total polymer solution. Further increase of ZnO-NPs number, agglomeration of particles was occurred and reduced the air-flux.

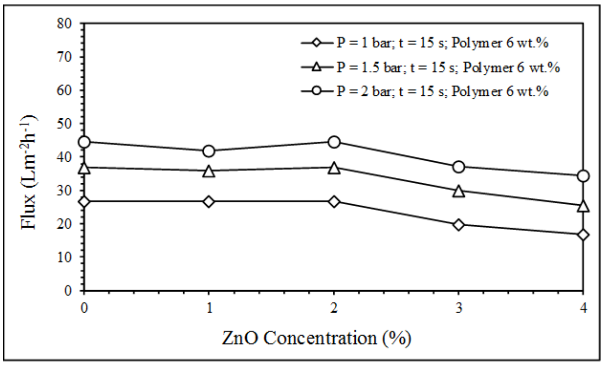


Figure 7. The influence of ZnO in coating solution on air flux at various operating pressures

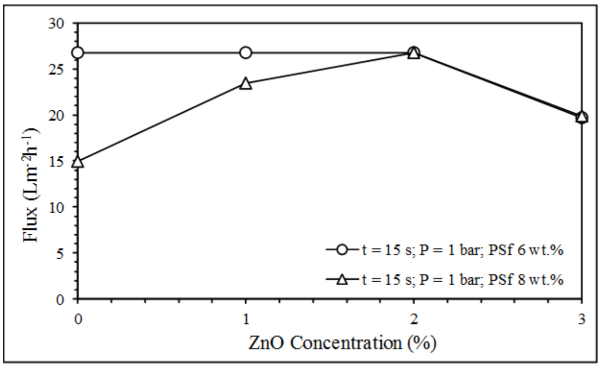


Figure 8. The influence of ZnO in coating solution at different polymer concentrations

III.5 The Influence of Coating Time on Particulate Removal

The filtration efficiency was decreased when the coating time was prolonged (Figure 9). It has been explained that the increase of coating time led to the formation of larger membrane pore. Consequently, particulate removal was decreased. It was found that the decrease of contaminants was between 50 - 65% when the coating time was prolonged from 2 to 10 s. The coating time of 2 s resulted in fine particles PM1 removal close to 60%. Meanwhile, the removal of particles PM2.5 and PM10 was around 50%. Further increase of coating time to 15 s, the particulate removal was decreased to 20 - 25% due to the large membrane pore size.

Conversely, the rejection of particulate was improved by increasing the operating pressure (Figure 10). The increase of permeation drag permeation through the membrane along with the raise of operating pressure enhanced the accumulation of contaminants on the membrane surface. The fouling formed on the surface acted as a second membrane layer that improved solute rejection. Higher rejection was achieved at an operating pressure of 2 bar. The rejection values of PM1, PM2.5, and PM10 were 70%, 74%, and 70%, respectively.

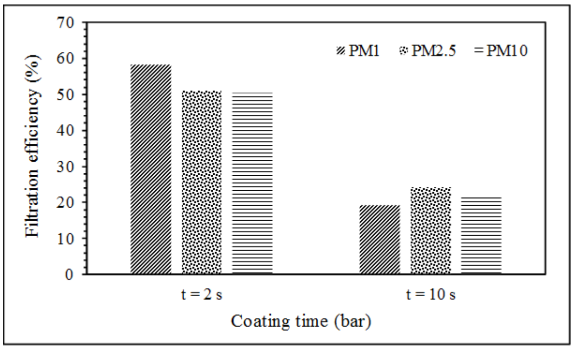


Figure 9. The influence of coating time on particulate removal at constant operating pressure (1 bar) and polymer concentration (6%).

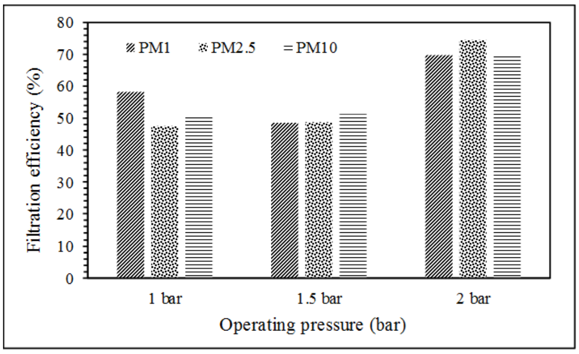


Figure 10. The influence of operating pressure on particulate removal at constant operating pressure (1 bar) and polymer concentration (6%).

IV. CONCLUSION

MPP membrane has been modified by coating the membrane surface with a composite PSf/PEG400/ZnO layer. The increase of polymer concentration from 6 to 8 wt.% reduces the permeate flux to 45%. The air flux was stable with the increase of polymer concentration when the ZnO-NPs are added into the coating solution.

The membrane performances are also influenced by coating time and operating pressure. The prolongation of coating time from 2 to 15 s enhances the air flux from 21 to 26 Lm-2h-1 and conversely, it reduces particulate rejection from 50 - 50% to less than 20 - 25%. The filtration efficiency was raised with the increase of the operating pressure. The particulate removal of PM1, PM2.5, and PM10 at an operating pressure of 2 bar were 70%, 74%, and 70%, respectively.

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