

EFFECT OF OPERATING PRESSURE ON PORE STRUCTURE STABILITY OF POLYPROPYLENE HOLLOW FIBER MEMBRANES EVALUATED BY POROMETRY

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ABSTRACT

This study evaluates the pore characteristics and structural stability of polypropylene (PP) hollow fiber membranes used in printed circuit board (PCB) wastewater treatment. A capillary flow porometer integrating gas–liquid and liquid–liquid displacement methods was applied to characterize pore size and pore size distribution for both pristine and field-used membranes, as well as under simulated flushing conditions. Field-used membranes exhibited larger pore sizes and broader distributions, which are associated with filtration history and possible improper cleaning operations involving elevated pressures. Repeated gas–liquid displacement measurements further showed variations in pore characteristics, suggesting sensitivity to applied pressure. The pristine membrane exhibited an average pore size of approximately 0.028 μm , consistent with manufacturer specifications, and only minor changes were observed under short-duration flushing at the design pressure (2.5 bar). However, increasing pressure and extending flushing duration resulted in noticeable pore enlargement and broader distributions, particularly under high-pressure backwashing conditions. These results indicate that PP hollow fiber membranes are sensitive to operating conditions, and excessive pressure may influence pore structure. The integrated porometry approach provides a consistent method for evaluating membrane properties across different conditions.

KEYWORDS:

Polypropylene hollow fiber membrane, Ultrafiltration, Forward-backward flush,
Pressure damage, Porometer

1. INTRODUCTION

The rapid expansion of the artificial intelligence (AI) industry has significantly increased the demand for AI servers, accelerator cards, and data centers, thereby driving the growth of the associated hardware supply chain. Printed circuit boards (PCBs) play a critical role in modern electronics by replacing bulky cabling, improving signal integrity, and enabling device miniaturization. PCB fabrication involves multiple processes and materials, including copper circuitry, vias, pads, solder masks, and surface finishes.

Solder masks, typically composed of photosensitive or thermosetting polymers, are applied to protect circuitry while exposing conductive pads. The process includes coating, exposure, development, and curing. During development, aqueous solutions containing 1–2% Na_2CO_3 are used to remove unreacted monomers, while defective boards may be treated with 3–5% NaOH for stripping. These processes generate high chemical oxygen demand ($\text{COD} > 10,000 \text{ mg/L}$) alkaline wastewater, commonly referred to as developer/ink-removal mixed wastewater. Effective pretreatment is required to remove suspended solids and polymer residues and to improve water recovery efficiency.

Microfiltration (MF) and ultrafiltration (UF) technologies are widely applied for such separations. Considering the alkaline environment, high organic loading, and economic constraints, polypropylene (PP) hollow fiber membranes are commonly employed in outside-in filtration configurations. However, membrane fouling remains unavoidable, leading to flux decline and increased transmembrane pressure. Routine cleaning through forward flushing (outside-in) and backwashing (inside-out) is therefore necessary. Due to the flexible and tough nature of PP materials, pressure fluctuations during these processes may induce pore deformation and enlargement, potentially compromising filtration performance.

Capillary flow porometry provides a quantitative method for characterizing membrane pore structures based on interfacial tension differences between wetting and displacing fluids. In this study, both gas–liquid and liquid–liquid displacement methods were applied to investigate the effects of cleaning pressure and duration on pore size evolution in PP hollow fiber membranes.

2. MATERIALS AND METHODS

A commercially available PP hollow fiber membrane was used in this study. In addition, membrane samples were collected from modules used in a PCB manufacturing facility after solder mask wastewater filtration. These used membranes were rinsed with water to remove surface fouling prior to analysis.

Membrane morphology was examined using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7610F). Prior to imaging, samples were immersed in liquid nitrogen and fractured to preserve and expose cross-sectional structures.

Pore size characterization and cleaning simulations were conducted using a capillary flow porometer (Innova UNP-1500, Poretech Instruments Inc.), capable of performing both gas–liquid and liquid–liquid displacement measurements over a pore size range of 2 nm to 500 μm . Hollow fiber samples with an effective area of approximately 4.08 cm^2 were mounted in a dedicated module. By adjusting module configuration, forward flushing (outside-in) and backwashing (inside-out) were simulated.

Flushing experiments were conducted using deionized water. The pressure was increased to 2.5 or 7.0 bar within 1 min and maintained for either 1 or 10 min. The pressure of 2.5 bar corresponds to the manufacturer-specified maximum operating pressure. Pore size and distribution were subsequently measured using the same instrument.

3. RESULTS AND DISCUSSION

As shown in Figures 1(a) and 1(b), the PP hollow fiber membrane was fabricated via a uniaxial stretching process, resulting in an anisotropic pore structure. The pores exhibit an elongated, elliptical morphology with a preferential orientation along the stretching direction. The surface pore size is approximately in the range of 0.1–0.5 μm .

In contrast, the hollow fiber membranes presented in Figures 1(c) and 1(d) were obtained from modules used for solder mask wastewater filtration under improper forward flushing and backwashing conditions. The operating pressure during these cleaning procedures reportedly exceeded 7 bar. A distinct fouling layer is observed on the outer surface of the hollow fiber membrane. In addition, the diameter of the hollow fibers after wastewater

filtration is significantly larger than that of the pristine membrane (approximately 260 μm), indicating that the membrane was subjected to external mechanical stress during filtration and improper cleaning operations. This suggests that the pore structure may have been damaged.

For these samples, cross-sectional pore morphology could not be readily characterized. Even after immersion in liquid nitrogen to preserve the structure, followed by mechanical fracturing, well-defined cross-sectional pore structures could not be obtained. Therefore, a capillary flow porometer was employed to analyze the pore size and pore size distribution of the hollow fiber membranes.

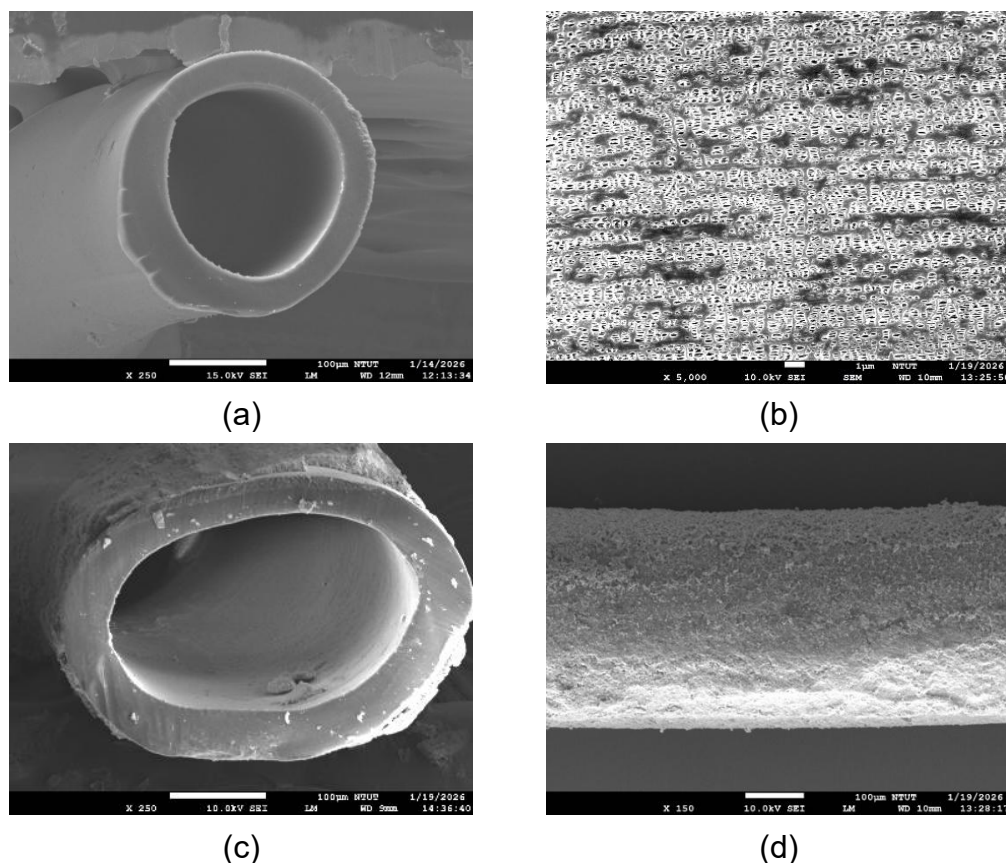


Figure 1. SEM images of PP hollow fiber membranes: (a) cross-section of the pristine membrane; (b) outer surface of the pristine membrane; (c) cross-section of the solder mask-fouled membrane; (d) outer surface of the fouled membrane.

The pore characteristics of the used hollow fiber membranes were analyzed using gas-liquid displacement method with three repeated measurements, and the results are shown in Figure 2. As illustrated in Figure 2(a), the dry-wet

curves obtained from the three measurements exhibit significant differences. The corresponding pore size distributions (Figure 2(b)) indicate that the pore size in the first measurement is approximately 0.2 μm . In contrast, during the second and third measurements, the pore size increases noticeably and the distribution becomes broader.

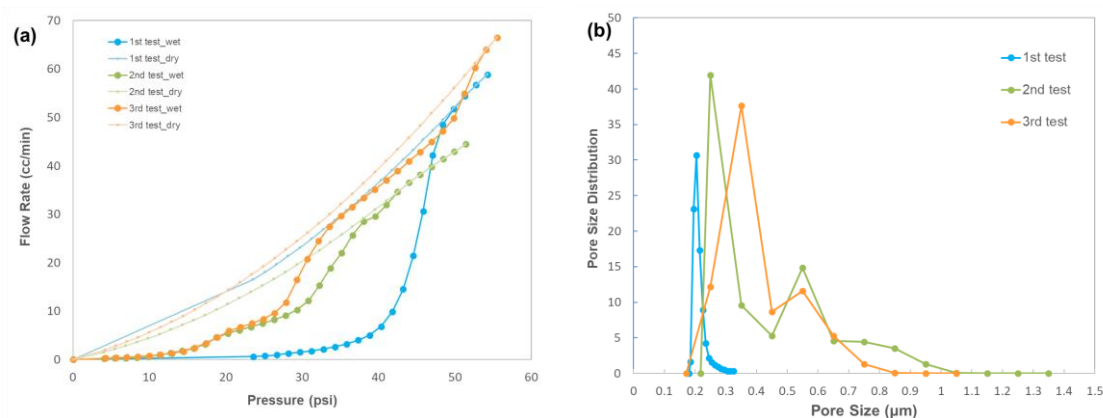


Figure 2. Repeatability test results obtained by gas–liquid displacement capillary flow porometry: (a) dry–wet curves; (b) pore size distributions.

To further clarify this behavior, the pristine hollow fiber membrane was characterized. As shown in Figure 3, the average pore size of the pristine membrane is approximately 0.028 μm , which is consistent with the specifications provided by the manufacturer and is significantly smaller than that of the membranes after wastewater filtration. After forward flushing and backwashing, although the flushing duration was only 1 min, a slight increase in pore size and broadening of the pore size distribution can already be observed. This indicates that the PP hollow fiber membrane is sensitive to operating pressure.

Compared with Figures 3(a) and 3(b), Figures 4(a) and 4(b) show that when the pressure holding time during forward flushing is extended to 10 min, the pore size increases significantly. Under a forward flushing pressure of 7 bar for 10 min, the pore size distribution further evolves into a bimodal distribution. In comparison with Figures 3(c) and 3(d), Figures 4(c) and 4(d) indicate that under backwashing at 2.5 bar, the change in pore size is not significant. However, when the pressure is increased to 7.0 bar and maintained for 10 min, a multi-modal pore size distribution appears. The primary pore size is centered at approximately 0.04 μm , which is close to that observed under forward flushing conditions. In addition, two broader secondary pore distributions are observed

at approximately 0.068 and 0.09 μm , which are closer to those of membranes subjected to solder mask wastewater filtration and improper cleaning procedures. It should be noted that the hollow fiber membranes used in field operations have undergone multiple filtration and cleaning cycles; therefore, the pore sizes observed in Figure 1 are significantly larger than those of membranes subjected only to simulated cleaning procedures without prior filtration.

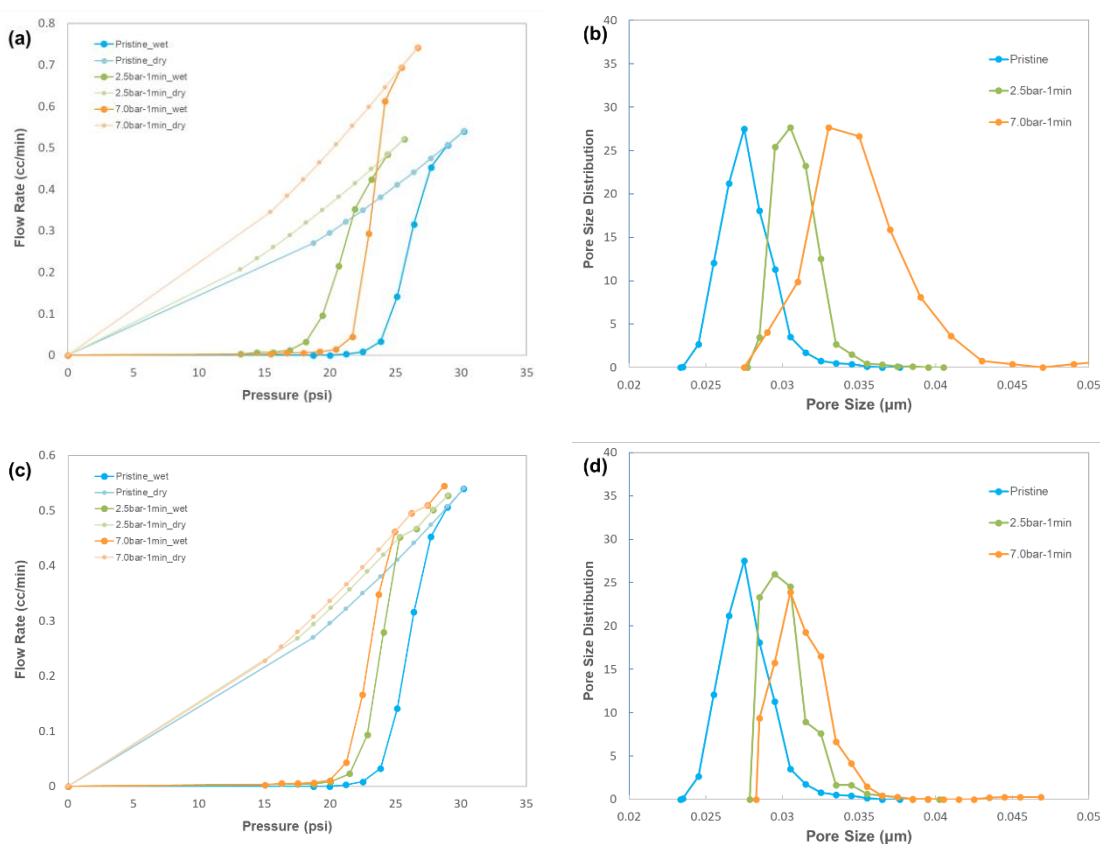


Figure 3. Effect of flushing pressure (1 min holding time) on dry–wet curves and pore size distribution measured by liquid–liquid displacement porometry. (a, c) Dry–wet curves; (b, d) pore size distributions. (a, b) Outside-in mode (forward flushing); (c, d) inside-out mode (backwashing).

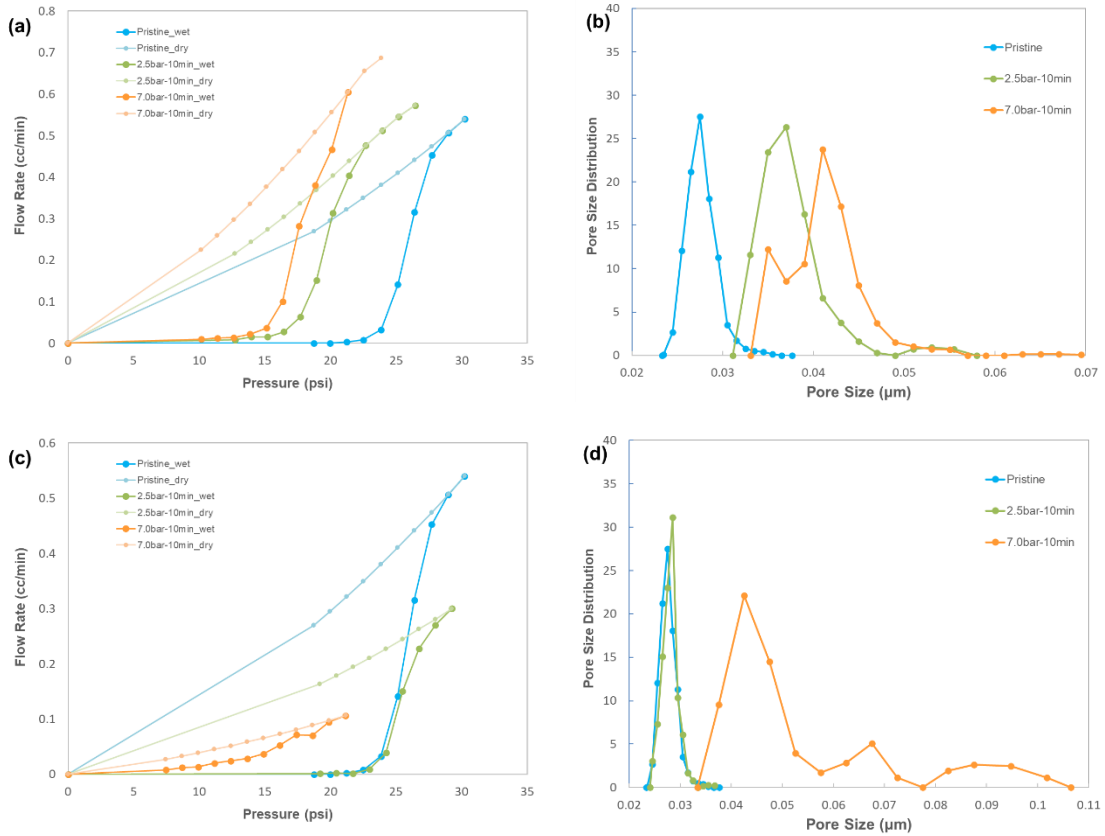


Figure 4. Effect of flushing pressure (10 min holding time) on dry-wet curves and pore size distribution measured by liquid-liquid displacement porometry. (a, c) Dry-wet curves; (b, d) pore size distributions. (a, b) Outside-in mode (forward flushing); (c, d) inside-out mode (backwashing).

Table 1 summarizes the mean flow pore diameter of PP hollow fiber membranes after forward flushing and backwashing. It is evident that the pore size increases after the cleaning procedures. Although hollow fiber membranes are generally considered to be self-supporting, the results of this study show that pore expansion still occurs after forward flushing at both 2.5 and 7.0 bar. Furthermore, extending the flushing duration leads to more pronounced pore enlargement.

At a flushing pressure of 2.5 bar, the variation in pore size after backwashing is relatively small compared with the pristine membrane. However, when the backwashing pressure increases to 7.0 bar, the mean flow pore diameter shows a more significant change compared with forward flushing. This suggests that, under inside-out pressurization, combined with the flexible and tough nature of PP material, the membrane may undergo deformation analogous to bursting, resulting in damage to the pore structure.

Table 1. Mean flow pore diameter under different flushing conditions.

Outside-in mode (Forward flush)				Inside-out mode (Back flush)		
Flushing time: 1 min.						
Flush Pressure (bar)	0	2.5	7.0	0	2.5	7.0
Mean Flow pore diameter (nm)	27.5	30.7	34.6	27.5	29.9	31.1
Flushing time: 10 min.						
Flush Pressure (bar)	0	2.5	7	0	2.5	7
Mean Flow pore diameter (nm)	27.5	36.7	41.1	27.5	28.1	51.1

4. CONCLUSIONS

In this study, a porometer was employed to analyze the pore size, pore size distribution, and material stability of PP hollow fiber membranes before and after filtration. For membranes subjected to field operation, pore size distributions measured by the gas–liquid displacement capillary flow method showed significant enlargement upon repeated measurements. When the operating pressure during pore measurement was comparable to the transmembrane pressure in practical filtration, repeated testing led to a clear increase in pore size and a broadening of the pore size distribution, indicating poor structural stability of the membrane pores.

The pristine PP hollow fiber membranes were further characterized using the liquid–liquid displacement capillary flow method. The results show that when the flushing pressure and duration are within the design limit (2.5 bar), only slight increases in pore size and distribution are observed. However, when the flushing pressure exceeds the design limit, both forward flushing and backwashing pressures, as well as extended backwashing duration, result in significant pore enlargement, broader pore size distributions, and the emergence of multi-modal distributions.

These findings demonstrate that integrating gas–liquid and liquid–liquid displacement methods into a single instrument enables consistent characterization of membranes over a wide pore size range using the same measurement principle under different modes. This approach also minimizes

measurement discrepancies that may arise from the use of different instruments.

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