Influence of Nanoimprint Lithography on Membrane Structure and Performance

Sajjad H. Maruf, Zhengwei Li, Joseph A. Yoshimura,
Jianliang Xiao, Alan R. Greenberg, and Yifu Ding*

*Membrane Science, Engineering and Technology Center and
Department of Mechanical Engineering,
University of Colorado, Boulder, CO 80309-0427, USA*

Abstract

Imparting sub-micron periodic patterns on the surface of ultrafiltration (UF) membranes has been shown to improve their antifouling characteristics. However, the deformation mechanism underlying membrane surface-patterning with nanoimprint lithography (NIL) is currently unclear. In response to this need, this study addresses the influence of nanoimprinting on the structural and performance characteristics of a commercial polyethersulfone (PES) UF membrane. The work utilized a flat (no pattern) as well as a pattern-containing mold such that local surface deformation associated with pattern formation could be isolated from the overall mechanical deformation in compression. The mechanical properties of the UF membrane as a function of temperature and deformation rate were characterized, and the overall thickness, molecular weight cutoff, and DI water permeance were measured for membranes imprinted using the flat mold. The data show that the influence of the NIL process on the membrane structure is length-scale dependent. Furthermore, imprinting of the UF membrane with the pattern-containing mold was examined experimentally as well as with finite element simulation. Results indicate that the non-uniform contact deformation at the membrane-mold interface provides the potential to optimize the NIL conditions for achieving desired pattern geometries without significantly increasing the membrane resistance.

Keywords: Porous membranes, Surface patterning, Permselective properties

* Corresponding author at :Department of Mechanical Engineering, 427 UCB, University of Colorado, 1111 Eng. Drive, Boulder, CO 80309-0427; Tel.: +1 303 492 2036; E-mail address: Yifu.Ding@Colorado.Edu; Fax: +1 303-492-3498.

1. Introduction

Membrane-based technologies are important for applications that include water purification, chemical and pharmaceutical separations, and energy production [1-4]. For liquid-based membrane separation processes, flux decline due to membrane fouling is a major concern and long-standing problem [5-8]. Over recent years a number of surface modification strategies based on both chemical and physical mechanisms have been employed to improve the antifouling characteristics of polymeric membranes [9-11]. Recently, we developed a method that can directly impart sub-micron surface patterns onto commercial ultrafiltration (UF) membranes [12, 13]. These patterned surfaces can further serve as a substrate for fabricating surface-patterned thin film composite membranes [14]. Previously reported results indicate that the presence of these surface patterns on the membrane significantly increases the critical flux, i.e. the flux above which irreversible fouling occurs, during filtration under varying conditions using different-sized silica particles [13, 15]. Furthermore, the surface patterns also reduce the irreversible deposition of proteins during filtration under different combinations of feed-solution chemistry (ionic strength and pH) as well as improved the flux recovery after post-filtration cleaning [12].

Successful surface patterning of a commercial polyethersulfone (PES) UF membrane was achieved using nanoimprint lithography (NIL), which is a simple and robust technique capable of fabricating sub-10 nm features at relatively low cost and high throughput [16-18]. For conventional NIL processes, the pattern replication mechanism is based on the “squeeze flow” of viscous polymer that is supported on a rigid substrate [19-21]. Specifically, a viscous polymer film is first squeezed into the nanoscale cavities of a rigid (silicon) mold under a relatively high pressure (a few MPa) at a temperature above the glass transition temperature (T_g) of the polymer, and then vitrified at a temperature below T_g before the release of pressure. However, imprinting polymeric membranes at a temperature higher than T_g causes the porous structure to collapse, despite excellent pattern replication. As a result, the surface-patterned membranes become impermeable at normal operational pressures, and thus ineffective for UF membrane separations.

In contrast, we found that successful surface patterning without significant pore sealing of the UF membrane could be achieved at a temperature below the T_g of the polymer [13]. Currently, the mechanical deformation mechanism(s) that contribute to the surface patterning

process at such low temperatures remain unclear. Such understanding is of critical importance for successfully applying NIL to a broad range of UF and microfiltration (MF) membranes that target specific applications. The subject study was designed to comprehensively characterize the mechanical behavior of a commercial PES UF membrane and systematically examine the influence of NIL processing conditions including, temperature, pressure and duration on the pore structure as well as the separation characteristics of the imprinted membranes. In addition, complementary finite element simulations were carried out to provide more insight regarding the mechanical deformation modes of the membrane during patterning.

2. Experimental

2.1. Materials

This work utilized the same commercial UF membrane (GE Osmonics) used in our previous patterning studies [12, 13]. The membrane consisted of an asymmetric PES porous layer atop a non-woven polyester web. The virgin flat-sheet membranes were stored in a dry, ambient environment and used in the as-received condition, i.e. no further treatments were applied before NIL processing, mechanical testing, and filtration measurements. Commercial UF membranes often contain organics such as glycerol to protect the pore-structures, which will only affects the mechanical responses of the membrane at much high strain rates compared with that used in this work. Our mechanical measurements showed that the elastic modulus of the membrane increased $\sim 6\%$ after DI water filtration, which confirms that glycerol, if present, has a negligible impact on the mechanical properties of the UF membranes.

2.2. Surface patterning

Surface patterning of the UF membranes was carried out using NIL with an Eitrie 3 nanoimprinter (Obducat, Sweden). As illustrated in Fig. 1, a silicon (Si) mold was brought into contact with the surface a UF membrane under constant temperature and pressure conditions causing the membrane to deform into the mold cavities. Upon releasing the pressure at a predetermined lower temperature, the pattern on the mold was replicated on the membrane surface. Two types of Si molds were used in this work: (1) a smooth and flat (featureless) Si wafer and (2) a Si wafer containing line-and-space grating patterns (periodicity = 575 nm, line

width = 210 nm, and groove depth = 180 nm). Each mold type was cleaned with a Nano-strip® solution (stabilized 3:1 concentrated sulfuric acid to hydrogen peroxide solution) prior to NIL processing. NIL imprinting conditions for the membranes were systematically varied using temperatures ranging from 40 °C to 180 °C, pressures between 1 MPa and 4 MPa, and times extending from 1 min to 7 min. For all samples, the demolding temperature was 40 °C.

Figure 1. Schematic illustration of surface patterning a UF membrane with NIL.

2.3. Mechanical characterization

The thermomechanical properties of the PES layer were systematically characterized using dynamic mechanical analysis (DMA, TA Instruments Q800). The porous PES layer (thickness: ~ 65 μm) was first separated from the supporting polyester web and cut into 15 mm $\times$ 6.5 mm rectangular specimens. Using DMA, the T_g of the PES layer was determined under tension with a dynamic loading frequency of 1 Hz and a strain amplitude of 0.1% while the temperature was increased from 30 °C to 250 °C at a controlled heating rate of 5 °C/min. The T_g value was defined as the temperature corresponding to the maximum of the $\tan \delta$ damping peak. Static tensile tests of the porous PES samples were also performed using the DMA to obtain isothermal stress-strain relationships for these samples at a constant strain rate. Measurements were carried out at 40, 80, 120 and 160 °C, and at each temperature tests were conducted at three strain rates: 0.001, 0.01, and 0.1 s^{-1} . A 10-min waiting period was adopted before each measurement to ensure that the temperature throughout the membrane sample reached the designated value. Three different specimens were tested at each condition (strain rate and temperature) so that a mean and standard deviation for each condition could be obtained.

Atomic force microscopy (AFM, DI 3100, Bruker) was used to characterize the surface topography of the imprinted membranes. The measurements were performed in tapping mode

under ambient conditions using a silicon cantilever probe. Cross-sectional images of the membranes were obtained using field-emission scanning electron microscopy (FESEM, Supra 60, Zeiss). The samples were prepared using a cryostat microtome (Leica CM1850), following embedding in Tissue-Tek® O.C.T. compound and freezing in dry ice. Each sample was washed with DI water to remove the embedding compound, dried, and then coated with a 4-5 nm gold layer prior to SEM imaging.

2.4. Performance and porosity measurement

All of the filtration experiments were conducted at room temperature in a dead-end, high-pressure stainless steel stirred cell (HP4750, Sterlitech) with an active membrane area of 14.6 cm². During filtration, permeate was weighed over timed intervals using an automated electronic balance (PI-225DA, Denver Instrument). For a given membrane sample, DI water (resistivity = 18.2 MΩ cm) flux was measured at three transmembrane pressures (TMP): 138, 207 and 276 kPa (Fig. 2). The steady-state flux at each pressure was obtained after the initial compaction period (~30 - 35% flux reduction over 2-3 h), and was defined as the point at which the flux varied less than 2% over the prior 10-min interval (Fig. 2 inset). The permeance of the membranes is reported as the slope of the linear flux-TMP plot (Fig. 2).

Figure 2. Steady-state permeate flux during DI water filtration at different TMP for a flat-wafer compressed UF membrane (120 °C, 2 MPa, 3 min). Error bars representing standard deviations are too small to be resolved. Inset: An example showing the time-dependent permeate flux of a membrane at a TMP of 276 kPa from which the steady-state flux was determined from the asymptotic value at 140-150 min.

Molecular weight cutoff (MWCO) values for the virgin and imprinted membranes were determined with size-exclusion chromatography (SEC, Agilent 1100, Agilent Technologies) using an aqueous solution of polyethylene glycols (PEGs) with varying molecular masses (100 – 25,800 g/mol, Sigma Aldrich). For a given membrane, the PEG solution (~ 1 g/ L) was filtered at ~207 kPa for 1 h while permeate was collected and recorded every 10 min. The molecular mass distributions in the feed and permeate solutions were measured via SEC with a silica column (Yarra SEC-3000, Phenomenex). The retention coefficients (R) for PEG with different molecular mass were determined as $R_{obs} = 1 - C_p/C_f$, where C_p and C_f represent permeate and feed concentration, respectively. Three measurements were conducted for each membrane sample, and the R_{obs} values are reported as mean $\pm$ standard deviation.

The porosity of the virgin PES porous layer was determined by measuring the difference in mass between the wet and dry PES layer. The membrane sample was filtered at 276 kPa for 20 min, and a membrane sample with an area of 9.7 cm² was then sectioned after filtration. The PES layer was immediately separated from the supporting web and immersed in DI water for about 14 h. After removing the excess water at the membrane surface by blotting with filter paper, the mass of the wet PES layer, w_1 , was measured. The mass of the dry PES layer, w_2 , was determined after drying in a vacuum oven at 30 °C for 24 h. The porosity of the PES layer was then determined as,

$$\epsilon = \frac{w_1 - w_2}{\rho A l} \quad (1)$$

where A and l are the area and thickness of the wet membrane, respectively, and ρ is the density of water (0.998 g/cm³). For the imprinted membranes, it proved challenging to separate a sufficiently large area of the PES layer from the support for porosity measurement. Instead, smaller strips of PES layers were detached from the substrate and the mean thickness value was used for the porosity calculation.

2.5. Finite element analysis

A plane-strain finite element model was established in ABAQUS to study the mechanical deformation during NIL processing of the porous PES membrane. A unit cell with periodic boundary conditions (PBCs) was adopted for the simulation due to the periodic nature of the surface pattern, and four-node, plane-strain elements (CPE4) were used to discretize the

membrane substrate. Since the silicon mold is much stiffer than the PES membrane, the mold is considered to be rigid, and thus its deformation is negligible. The crushable foam plasticity model was used to characterize the material behavior of the PES membrane. The simulation focused on examining the influence of imprinting pressure on membrane deformation at 120 °C. The stress-strain behavior of the PES membrane under compression at 120 °C was defined based on the tensile test data given the difficulty in obtaining accurate values in compression for thin films.

3. Results and discussion

3.1. Mechanical behavior of the PES membrane

Based on DMA measurements, the T_g of the PES UF membrane was ~215 °C, which agrees well with the value reported in the literature for bulk PES [22]. Our prior work showed that imprinting of UF membranes must be carried out at temperatures below T_g to avoid detrimental pore-sealing that would result in an impermeable membrane. Thus, optimization of the NIL process at such sub-critical temperatures requires a thorough understanding of membrane mechanical behavior. However, direct measurement of large compressive deformation on a thin porous membrane under appropriately controlled conditions is quite challenging. Given that polymer stiffness and yield characteristics are generally similar in tension and compression [24], simpler-to-conduct tensile tests of the PES layers were carried out at different combinations of temperature and strain rate that are relevant to the NIL process.

Figure 3. (a) Representative stress-strain curves of the PES layer during tensile tests at different temperatures at a strain rate of 0.01 s^{-1} ; The dashed line represents a 2% offset to estimate the yield strength of the sample at 40°C . (b) Offset yield strength of the PES layer as a function of temperature at three different strain rates. Each datum represents the mean value of three independent samples, and the error bars provide the corresponding standard deviation, which is sufficiently small in most cases that the error bars are hard to resolve. Yield strength values for bulk PES from ref. [23] are also plotted for comparison (filled squares).

Figure 3a shows representative stress-strain curves for the PES layer (without the backing web) obtained from tensile tests at $40, 80, 120$ and 160°C at a strain rate of 0.01 s^{-1} . The stress-strain curves of the PES layer resemble those of classical cellular solids such as metal or polymeric foams [24-27]: a linear elastic response at low strains (2 - 3%), an extended plateau region (20 - 30%) after apparent yielding, and finally brittle failure of the sample. Normally, the linear elasticity of a porous glassy film is dictated by the bending/twisting of the cell walls [24]. By approximating the porous PES layer as an open-pore cellular solid, the Young's modulus (E^*) of the porous PES layer can be estimated from [24],

$$E^* = E_o C_1 \left(\frac{\rho^*}{\rho_o} \right)^2 \quad (2)$$

where ρ^* is the effective density of the porous membrane, C_1 is a constant ranging from 0.3 - 1, and E_o and ρ_o are the Young's modulus and density of the bulk PES, respectively. Using the result at 40°C and 0.01 s^{-1} as an example, E^* of the PES membrane was measured to be 0.16 GPa from the slope of the stress-strain curve in the linear elastic region. From ref.[23], E_o at 40°C is $\sim 2.39 \text{ GPa}$ under the same stain rate. Using Eq (2), the effective porosity of the PES layer ($1-\rho^*/\rho_o$) is estimated to be 53% - 74%, with C_1 ranging from 0.3 – 1.

The yield strength of the PES porous layer, σ_y^* , can be determined from the stress-strain curves using the 2% off-set convention [28]. Evidently, even at a temperature as low as 40°C , the PES membrane yields at a tensile stress of $\sim 4.2 \text{ MPa}$. Prior work has shown that plastic deformation for porous glassy polymer films can occur at a relatively low stress (several MPa) when the porosity is high [13, 29]. Plastic deformation of the membrane is caused by the rotation/twisting of cell walls/edges towards the tensile axis. Once rotation of these structural units cease, further tensile loading leads to stretching of these now oriented cell walls. When the cell walls consist of viscoelastic materials such as PES, they also experience the effect of stress-

concentrations and are under much higher effective loading which causes local yielding. Therefore, much of the plastic deformation of the porous membranes is not recoverable, and the membrane pore structure is permanently altered.

Approximating the PES porous layer as an open-cell foam, σ_y^* of the PES layer can also be estimated empirically as [24],

$$\sigma_y^* = \sigma_{y,0} C_2 \left(\frac{\rho^*}{\rho_0} \right)^{3/2} \quad (3)$$

where $\sigma_{y,0}$ is the yield strength of the bulk PES and C_2 is a constant ranging between 0.2 - 0.3. Again, using the combination of 40 °C and 0.01 s⁻¹ as an example, $\sigma_y^* = 4.2$ MPa from our measurement and $\sigma_{y,0} = 78.9$ MPa from ref.[23]. In addition, the effective porosity of the PES layer is estimated to range from 59 % to 68 %, when $C_2 = 0.2 - 0.3$. This porosity range agrees reasonably well with the above effective porosity estimation based on elasticity values. In comparison, the porosity directly measured from the sorption/desorption method (~ 56 %) appears to match the lower limit of the estimations based on Young's modulus and the yield strength. It is likely that the measured porosity is underestimated due to the lack of complete pore filling as well as some modest mass loss despite careful weighing of the wet samples.

Fig. 3b summarizes the σ_y^* values for the PES porous layer obtained at different temperature and strain rate combinations with those for bulk PES as a function of temperature at a constant strain rate of 0.01 s⁻¹ [23]. The results show that σ_y^* of the PES membrane decreases with increasing temperature and decreasing strain rate, which is similar to the trend observed in bulk polymers [30]. The rate dependence of the mechanical responses for viscoelastic cellular foams can be primarily attributed to the: (1) rate of buckling of the cell walls, and (2) yielding of the cell wall material. Clearly, the intrinsic rate dependence of polymer yielding is the rate-limiting factor as it is expected to be much slower than the rate of cell wall buckling. Within the range of strain rates used in the subject experiments, yielding and the rate of plastic deformation for the membrane are indeed dictated by that of the PES walls between neighboring pores.

Prior studies have shown that while both elastic modulus and yield strength under uniaxial compression are somewhat smaller than values obtained under uniaxial tension, the major difference between the two types of deformation lies in the fracture behavior [24, 31]. Under tensile loading, brittle failure is commonly observed due to catastrophic propagation of

cracks (the fracture points are marked as “x” in Fig. 3a). Note that the trend observed in Fig. 3a, i.e. fracture strain decreases with increase of temperature is not representative for porous membranes. Similar to bulk materials, the fracture of porous membranes is dictated by the largest structural flaws (in this case, the largest macrovoids). The trend observed in Fig. 3a is most likely attributed to the presence of larger macrovoids in the samples measured at higher temperatures. Such brittle fracture will not occur under uniaxial compression. Instead, a densification stage (i.e. stress increase with increase of strain) usually follows the stress plateau, which is related to the collapse/contact of the cell walls that prevents further plastic deformation [24, 27].

3.2. NIL processing with a flat wafer

During the imprinting process (Fig. 1), the membrane is effectively compressed under normal pressure, whereas the deformation at the mold/membrane interface is most likely inhomogeneous because of the topographic features on the mold. Figure 4a shows a cross-sectional SEM image of the virgin membrane atop a non-woven support. The membrane features an asymmetric pore structure that includes a surface selective layer ($< 1\ \mu\text{m}$), an intermittent spongy layer ($2\text{--}7\ \mu\text{m}$), and a layer of macrovoids with a pore size on the order of tens of microns. Such a hierarchical structure is typical for UF membranes that were prepared via standard phase inversion processes [32]. After imprinting with a patterned mold at $120\ ^\circ\text{C}$ at $4\ \text{MPa}$ for 3 min, a grating pattern was successfully replicated on the top surface of the membrane (Fig. 4b inset). The image indicates that many of the “finger-like” macrovoids were apparently collapsed into much smaller micron-sized voids as a result of the imprinting. As a result, the overall thickness of the membrane was reduced from $\sim 65\ \mu\text{m}$ to $\sim 30\ \mu\text{m}$, i.e. a permanent deformation of $\sim 54\ \%$.

In order to better assess the effect of compression on the membrane pore structure without complexities arising from topography-induced stress concentrations, initial experiments were conducted using a flat, smooth wafer that provided uniform uniaxial compression of the membrane. Under identical patterning conditions ($120\ ^\circ\text{C}$ at $4\ \text{MPa}$ for 3 min), permanent compressive deformation characterized by flattened macrovoids similar to that in Fig. 4b was observed (Fig. 4c). Based on the successful use of the flat, smooth wafer to generate the overall mechanical response and corresponding structural changes of interest, we conducted a systematic

set of experiments to characterize the flat-wafer-compressed PES membranes under NIL-relevant time-temperature-pressure conditions.

Figure 4. Representative cross-sectional images of (a) the virgin PES UF and (b) a PES membrane compressed by a pattern-containing mold at 120 °C, 4 MPa and 3 min; and (c) a PES membrane compressed by a flat wafer at 120 °C, 4 MPa and 3 min. The inset in (b) shows the topographic AFM image of the imprinted surface with a pattern height ~ 63 nm.

First, we examined the DI water permeance of the membranes imprinted at six temperatures and four imprinting times at pressures of 2 MPa (Fig. 5a) and 4 MPa (Fig. 5b). At each combination of pressure and temperature, the permeance of the membranes (normalized by that of the virgin membrane) decreased when the imprinting time increased from 1 min to 3 min with a maximum decrease of about 25% (170°C, 4 MPa). However, further increases in imprinting time from 3 min to 7 min did not lead to significant changes in DI water permeance. DI water permeance is typically controlled by the pore structure (size, porosity, and tortuosity) and thickness of the membrane [33]. Based on a Hagan-Poiseuille-type relationship for liquid flowing through cylindrical pores, the permeance (and membrane resistance) is dictated by the pores with the smallest radius [34,35]. For the PES membranes used here, the resistance of the selective layer will be the most significant component in the overall resistance to DI water permeation, while the underlying layers primarily contribute mechanical support. The “skin” can be defined to include both the surface selective layer and the spongy layer such that their combined thickness is taken as the effective length scale for mass transport through the UF membrane [36].

Figure 5. DI water permeance (normalized by the value of the virgin membrane) of the membranes as a function of imprinting temperature and time at pressures of (a) 2 MPa and (b) 4 MPa. Each datum represents the mean value of three independent samples, and the error bars provide the corresponding standard deviation. The standard deviations are sufficiently small in most cases that the error bars are not resolved.

Given the relationship between DI water permeance and the membrane pore structure, the imprinting time-dependence of the permeance can be largely attributed to rate-dependent deformation in the selective layer during NIL processing. Approximating the PES membrane structure as an open-cell foam, the selective-layer creep strain under steady uniaxial stress, σ , is [24],

$$\epsilon = \frac{\sigma}{C_3(\rho^*/\rho_0)^2} \frac{E_{s1} + E_{s2}}{E_{s1}E_{s2}} \left(1 - \exp\left(-\frac{E_{s2}t}{\eta_s}\right) \right) \quad (4)$$

where C_3 is a constant with a value of ~ 1 , E_{s1} is the unrelaxed modulus of the solid, $E_{s1}E_{s2}/(E_{s1} + E_{s2})$ is the relaxed modulus, and η_s is the effective viscosity of the polymer. This relationship enables the creep strain to reach a steady state value when $t > \eta_s / E_{s2}$. The experimental results suggest that an imprinting time of 3 min appears sufficient for the PES selective layer to deform such that a steady-state morphology is obtained at the various temperature-pressure combinations. Hence, a 3-min imprinting time was used for all subsequent imprinting experiments.

Figure 6. DI water permeance of the flat-wafer-imprinted PES membranes as a function of imprinting pressure at different temperatures. All membranes were imprinted for 3 min. Each datum represents the mean value of three independent samples, and the error bars provide the corresponding standard deviation.

Figure 6 summarizes the normalized water permeance values for all of the samples imprinted with a flat wafer for 3 min under various pressure and temperature combinations. At each temperature the decrease of permeance with increasing pressure is reasonably linear with the dependence becoming more pronounced at higher temperatures. Given the expected inverse relationship between permeance and creep, the observed pressure dependence supports the assumption of linear viscoelastic compressive creep, at least of the selective layer which most influences membrane permeance. As indicated by Eq. (4), the compressive creep strain increases with increasing pressure. Both E_{s1} and E_{s2} in Eq. (4) have a strong inverse dependence on temperature, which results in a more pronounced pressure-dependence of the permanent deformation at higher temperature. This deformation behavior is reflected in the proportionally greater reduction of DI water permeance at higher temperature (Fig. 6).

As reported in the literature, open-cell cellular solids normally display lower yield strength under uniaxial compressive loading in comparison to that under uniaxial tensile loading [31, 37]. For example, measurements by Deshpande et al showed that the compressive yield strength of polymer foams was $\sim 60\%$ that of the tensile yield strength [31]. For the asymmetric PES membranes with anisotropic macrovoids (Fig. 3a), the yield strength when loaded along the “rise” direction (normal to the membrane surface) will be further lowered compared with that in

the in-plane direction (in parallel to the membrane surface). Both factors suggest that the PES membranes under uniaxial compression would evidence a much lower yield strength compared with that observed during the tensile test. Under uniaxial tension, the yield strength of the PES layer at 40 °C was ~ 4.2 MPa at a strain rate of 0.01 s^{-1} . It is most likely that at all imprinting temperatures, even the lowest pressure (1 MPa) applied is at or above the yield strength of the PES layer. It is important to note that such high values of applied stress during loading would normally lead to non-linear viscoelastic creep of the porous materials [24]. We speculate that the linearity observed in Fig.6 reflected the short-term nature of the loading such that non-linear creep behavior would become evident at extended time scales. However, we did not evaluate behavior in this regime since there seems no advantage in NIL processing over much longer durations.

Figure 7a presents the thickness of the PES layer (without the backing) after imprinting the membrane for 3 min at eight different temperature and pressure combinations. The virgin membrane had a PES layer thickness of $\sim 65 \text{ }\mu\text{m}$, corresponding to an overall measured porosity $\sim 56\%$. As noted previously, this value is at the lower range of the porosity estimated from the Eqn. 3, but most likely underestimates the true porosity. As expected, the thickness of the PES layer decreased with an increase of imprinting temperature and pressure (Fig. 7). For highly porous membranes, the change in porosity (or volume) should reasonably correlate with the change in thickness during compression, since the Poisson's ratio of these membranes is negligible. Using the results from the sample imprinted for 3 min at 120 °C and 4 MPa as an example, the thickness of PES layer was reduced from $\sim 65 \text{ }\mu\text{m}$ to $\sim 30 \text{ }\mu\text{m}$, i.e. a decrease in thickness of $\sim 54\%$, which is consistent with that observed from the cross-sectional SEM images shown in Fig. 4. Given the expected correlation between thickness and porosity changes, the latter should also decrease by $\sim 54\%$, which is clearly much larger than the percentage reduction in DI water permeance for the same membrane ($\sim 15\%$). This discrepancy highlights the fact that the DI water permeance is dictated by the smallest pores within the selective layer rather than the overall porosity.

Figure 7. (a) Thickness and (b) MWCO values after imprinting the PES membrane for 3 min at different combinations of temperature and pressure. Note that the thickness was measured after removal of the backing layer. Each datum represents the mean value of three independent samples, and the error bars provide the corresponding standard deviation.

To examine the changes in the smallest pores in the selective layer, we measured the MWCO of the membrane using PEG as a penetrant. Figure 7b shows the MWCO of membranes imprinted at different temperature and pressure combinations for 3 min with a flat wafer. The MWCO of the virgin membrane was ~ 15.4 kg/mol, which monotonically decreased with an increase of imprinting temperature and pressure. The radius of gyration of a polymer chain, R_g , is related to the molecular mass, M , in a good solution as $R_g \sim M^{0.6}$. Thus, the expected percentage reduction in the selective layer pore size would be $\sim 18\%$ for membrane imprinted at $120^\circ\text{C}/4\text{ MPa}/3\text{ min}$, which is much smaller than that the percentage of reduction in overall film thickness (or porosity, Fig. 7a), but comparable with the reduction in DI water permeance (Fig. 6).

3.3. NIL processing with a patterned wafer

A Si mold containing a parallel line-and-space grating pattern was used to imprint the PES membranes. The geometric parameters of the pattern included a periodicity of 575 nm, a line width of 210 nm, and a groove depth of 180 nm. Membranes were imprinted for 3 min at different combinations of temperature (80, 120, 140, 160 and 175°C) and pressure (2 and 4 MPa). Results for each combination are shown in Fig. 8 where at each pressure an increase in imprinting temperature provided an increase in AFM-measured pattern height but a decrease in

DI water permeance. However, the relative changes in the magnitude of these characteristics are rather different as the imprinting pressure increases from 2 to 4 MPa. For example, at 120 °C, a 125% increase in pattern height with only a corresponding 4% decrease in permeance was obtained by imprinting at the higher pressure. This relatively modest percentage decrease in permeance at 120 °C at 4 MPa was similar to that observed using the flat platen at the same conditions (Fig. 5). However, the results also indicate a much more pronounced decrease in permeance at imprinting temperatures above 120-140 °C (Fig. 8). Thus, there may well be a practical permeance-determined upper limit for NIL temperature and pressure combinations despite better pattern replication at such processing conditions.

Figure 8. Pattern height (solid symbols) and DI water permeance (open symbols) of the PES membranes after imprinting with a surface-patterned mold for 3 min at five different temperatures at pressures of (a) 2 MPa and (b) 4 MPa. Dotted lines represent the DI water permeance of the virgin membrane. Each data point was result of a single sample (non-replicated) measurement.

Our recent work has shown that taller patterns (with the same periodicity and line width) have improved antifouling characteristics [15]. The results presented in Fig. 8 provide a framework for selecting NIL processing parameters to achieve desired pattern quality (here represented by height) and permselective properties of the membranes. For example, PES membranes imprinted at 120 °C/4 MPa/3 min and 140 °C/2 MPa/3 min show similar DI water permeance, but significantly different pattern quality corresponding to pattern heights of ~63 and 33 nm, respectively.

To better understand the relationship between mechanical deformation and the resulting surface patterns, finite element analysis (FEA) was employed. Specifically, we simulated the bulging height of the membrane into the cavity as a function of imprinting pressure at 120 °C (Fig. 9). The simulation results were obtained based on input values that included an experimentally measured Young's modulus (130 MPa) and yield strength (~3 MPa) under tension, porosity of 56%, Poisson's ratio of 0, and a densification strain under compression (ϵ_D) of 38% that was estimated from the porosity according to $\epsilon_D = 1 - 1.4 \left(\frac{\rho^*}{\rho_0} \right)$ [24].

Figures 9. The contours of normal stress in the vertical direction of a deformed PES membrane under applied pressure of (a) 2 MPa and (b) 4 MPa; (c) bulging height as a function of applied pressure at 120 °C.

Figure 9a shows an example of the membrane deformation and the corresponding normal stress contour generated using an applied pressure of 2 MPa. The simulation results indicate that the membrane in contact with the mold interface as well as in regions away from the interface experience a normal stress that is higher than the applied load because of the reduced contact area. However, the portion of the membrane that bulged into the mold cavity evidenced normal stress loading that was considerably less than 2 MPa. At an applied pressure of 4 MPa, the compressive stress was again higher than that applied, and more of the membrane bulged into the cavity (Fig. 9b). Despite the difference in absolute magnitude, the stress distribution relative to the higher applied value appeared similar to that at 2 MPa. Note that the material bulging into the mold cavity and characterized by its height (bulging height) evidences both elastic and plastic

deformation; however, only the plastic component contributes to the creation of a permanent surface pattern after the pressure is released. Since the elastic strain is negligible, the final pattern height after pressure release should be comparable with the bulging height. Overall, the simulation analysis indicates that imprinting results in non-uniform membrane deformation with more extensive structural change in the contact regions but less on the material within the mold cavities.

While Fig. 9c shows that the bulging height increases with imprinting pressure at 120 °C, it should be noted that the dependence is nonlinear. Indeed, the predicted bulging heights at imprinting pressures of 2 and 4 MPa were ~ 26 and ~ 62 nm, respectively, which agree quite well with the corresponding experimental values of 28 and 63 nm. At low pressures (i.e. below the yield strength of the membrane, ~ 1.8 MPa), small bulge heights that are weakly dependent on the pressure were generated; at applied pressures above yielding (1.5 - 3 MPa), an approximately linear pressure dependence is observed. Above 3 MPa, weak pressure dependence is observed, corresponding to membrane densification in the region near the contact interface. These results suggest that an imprinting pressure with a magnitude between that of the yield and densification stresses produce an optimum result.

From Fig. 9, it is clear that pattern formation is mostly dictated by the compressive deformation of the membrane in the region beneath the mold interface, which forms the “valleys” of the pattern. Measurements on the flat-wafer compressed membranes (Fig. 6 and 7) indicate that the membrane resistance in these deformed regions should increase. In contrast, the ridges of the patterns experience relatively low stresses during imprinting such that membrane resistance in these regions might well be only minimally affected. As a result, increasing imprinting pressure (e.g. 2 to 4 MPa at 120 °C, Fig. 8) could significantly increase pattern quality (i.e., height) but only modestly affect overall resistance of the patterned membranes. Work to test this hypothesis regarding optimum NIL processing is currently underway.

4. Conclusion

In this work we characterized the mechanical properties of a commercial UF PES membrane that has been used previously as a platform for surface patterning via nanoimprint lithography (NIL). Based upon tensile test results, the elastic and yield behavior of the

membrane can be reasonably described by relationships developed for open-pore cellular solids. Of particular importance with respect to the NIL process, results show that the yield stress of the PES membrane decreases with increasing temperature and decreasing strain rate, in keeping with the trend observed for bulk polymers.

When imprinted (i.e., compressed) with a flat wafer, DI water permeance, PES porosity (represented by the thickness) and the MWCO of the membrane all decreased as a function of increasing imprinting temperature and pressure. For a UF membrane with a hierarchical structure such as the one used here, the influence of the NIL process on the pore structure is length-scale dependent. The virgin membrane has a bilayer skin and a macrovoid layer where the latter has higher porosity with much larger anisotropic pores. Upon imprinting, the macrovoids are essentially crushed such that there is a large reduction in overall PES thickness and porosity. Moreover, as inferred from the permeance and MWCO measurements, the smallest pores in the skin evidence less plastic deformation as compared with the macrovoids.

When imprinted with a patterned mold, the stress distribution and deformation at the mold/membrane interface appear highly non-uniform based upon results obtained from finite element analysis. Insights gained from this study provide a better understanding of the relationship between mechanical deformation and the surface patterning process, and suggest that the NIL conditions can be optimized to achieve higher quality patterns without significantly increasing membrane resistance.

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References

- [1]. Greenlee LF, et al., *Reverse osmosis desalination: Water sources, technology, and today's challenges*. Water Research 2009;43:2317-48.
- [2]. Pendergast MM, Hoek EMV, *A review of water treatment membrane nanotechnologies*. Energy & Environmental Science 2011;4:1946-71.
- [3]. Pinnau I, Freeman BD, *Formation and modification of polymeric membranes: Overview*, in *membrane formation and modification*. 1999; American Chemical Society. Chapter 1. 1-22.
- [4]. Qu X, Alvarez PJJ, Li Q, *Applications of nanotechnology in water and wastewater treatment*. Water Research 2013;47:3931-46.
- [5]. Antony A, et al., *Scale formation and control in high pressure membrane water treatment systems: A review*. J Membr Sci 2011;383:1-16.
- [6]. Field R, *Fundamentals of fouling*. In K.-V. Peinneman, S.P. Nunes (Eds.) *Membranes for water treatment*, Vol 4, Wiley-VCH. Weinheim. 2010;1-23.
- [7]. Goosen MFA, et al., *Fouling of reverse osmosis and ultrafiltration membranes: A critical review*. Separation Science and Technology 2005;39:2261-97.
- [8]. Kujundzic E, Greenberg AR, and Peterson M, *Ultrasonic characterization of membranes*. Desalination and Water Treatment 2014;52:1217-49.
- [9]. Khulbe KC, Feng C, and Matsuura T, *The art of surface modification of synthetic polymeric membranes*. J Appl Polym Sci 2009;115:855-95.
- [10]. Rana D, and Matsuura T, *Surface modifications for antifouling membranes*. Chem Rev 2010;110:2448-71.
- [11]. Reddy AVR, et al., *Surface modification of ultrafiltration membranes by preadsorption of a negatively charged polymer: I. Permeation of water soluble polymers and inorganic salt solutions and fouling resistance properties*. J Membr Sci 2003;214:211-21.
- [12]. Maruf SH, et al., *Influence of sub-micron surface patterns on the deposition of model proteins during active filtration*. J Membr Sci 2013;444:420-8.
- [13]. Maruf SH, et al., *Use of nanoimprinted surface patterns to mitigate colloidal deposition on ultrafiltration membranes*. J Membr Sci 2013;428:598-607.
- [14]. Maruf SH, et al., *Fabrication and characterization of a surface-patterned thin film composite membrane*. J Membr Sci 2014;452:11-19.
- [15]. Maruf SH, et al., *Critical flux of surface-patterned ultrafiltration membranes during cross-flow filtration of colloidal particles*. J Membr Sci 2014;471:65-71.
- [16]. Chou SY, Krauss PR, and Renstrom PJ, *Imprint lithography with 25-nanometer resolution*. Science 1996;272:85-7.
- [17]. Guo LJ, *Nanoimprint lithography: Methods and material requirements*. Adv Mater 2007;19: 495-513.
- [18]. Moore GE, *Cramming more components onto integrated circuits*. Proceedings of the IEEE 1998;86:82-5.
- [19]. Ding Y, et al., *Nanoimprint lithography and the role of viscoelasticity in the generation of residual stress in model polystyrene patterns*. Adv Funct Mater 2008;18:1854-62.
- [20]. Ding Y, et al., *Polymer viscoelasticity and residual stress effects on nanoimprint lithography*. Adv Mater 2007;19:1377-82.
- [21]. Ding Y, et al., *Relaxation behavior of polymer structures fabricated by nanoimprint lithography*. ACS Nano 2007;1:84-92.

- [22]. Sen AK, Kandpal LD, Mathur GN, *Proceedings of recent advances in polymers and composites*. 2000: Allied Publishers.
- [23]. Plummer CJG, and Donald AM, *The ductile–brittle transition in macroscopic tensile tests on polyethersulfone*. J Appl Polym Sci 1990;41:1197-212.
- [24]. Gibson LJ, Ashby MF, *Cellular solids: Structure and properties*. 1999: Cambridge University Press.
- [25]. Linul E, et al., *Study of factors influencing the mechanical properties of polyurethane foams under dynamic compression*. J Phys: Conference Series 2013;451:012002.
- [26]. Ashby MF, *The properties of foams and lattices*, Phil Trans A 2006;364:15-30.
- [27]. Avasle M, Belingardi G, and Montanini R, *Characterization of polymeric structural foams under compressive impact loading by means of energy-absorption diagram*. Inter J Impact Eng 2001;25:455-72.
- [28]. *Handbook of Polymer Science and Technology*. 1989: Taylor & Francis.
- [29]. Lee, JH, et al., *Enhanced energy dissipation in periodic epoxy nanoframes*. Nano Lett 2010;10:2592-7.
- [30]. Ward IM, Sweeney J, *An introduction to the mechanical properties of solid polymers*. 2nd Ed., 2005: Wiley.
- [31]. Deshpande VS, and Fleck NA, *Multi-axial yield behaviour of polymer foams*. Acta Materialia 2001;49: 1859-66.
- [32]. Van de Witte, et al., *Phase separation processes in polymer solutions in relation to membrane formation*. J Membr Sci 1996;117:1-31.
- [33]. Lalia BS, et al., *A review on membrane fabrication: Structure, properties and performance relationship*. Desalination 2013;326:77-95.
- [34]. Zeman LJ, Zydney AL, *Microfiltration and ultrafiltration: Principles and applications*. 1996: Taylor & Francis.
- [35]. Mehta A, Zydney AL, *Permeability and selectivity analysis for ultrafiltration membranes*. J Membr Sci 2005;249:245-9.
- [36]. Khayet M, Matsuura T, *Membrane distillation: Principles and applications*. 2011: Elsevier.
- [37]. Walter TR, Richards AW, Subhash G, *A unified phenomenological model for tensile and compressive response of polymeric foams*. J Eng Mater Tech 2008;131:011009.