Tolerance of Polymer-Zeolite Composite Membranes to Mechanical Strain

*Subhrakanti Chakraborty[‡], Bo Wang[‡], Prabir K. Dutta**

Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue,
Columbus, Ohio 43210.

*** Corresponding author Email: dutta@chemistry.ohio-state.edu**

ABSTRACT: Numerous studies have been reported for zeolite membranes grown on inflexible supports, such as alumina and metals, and examined for gas transport measurements. Polymer membranes are also used for gas separations, and have a far greater practical impact, primarily because of lower cost. Polymer membranes are made by rapid roll to roll methods, and large quantities can be generated, whereas zeolite membranes are typically made in a batch fashion at much smaller sizes. Because the mechanism of gas transport between zeolites and polymers is different, zeolite membranes have certain performance advantages. Combining the attributes of both zeolites and polymers in a membrane is of significant interest. In this paper, we examine two types of zeolite polymer membranes based on faujasitic zeolites, one with zeolite grown on top of porous polyethersulfone (Type I), and the second where the zeolite is grown within the pores of the porous polymer (Type II). We have previously reported that both Type I and II membranes perform satisfactorily for CO₂/N₂ separation. However, Type I membranes' performance is less reproducible and more sensitive to handling. In this study, we explore the elastic properties of these two types of membranes using Peak Force Quantitative Nanomechanical Measurement (PFQNM) technique by Atomic Force Microscopy. It is found that Type II membranes have lower elastic modulus even though the zeolite thickness in these membranes exceeds those of Type I membranes by an order of magnitude. Mechanical stress leads to cracks within the zeolite layer for both types of membranes, though Type II membranes tolerate higher stress. We propose that the higher stress-resistance of the Type II membranes arises because the polymer surrounding the zeolite acts to arrest the crack propagation. The genesis of cracking and elastic property measurements by AFM will be relevant for other polymer-inorganic composites, where an inorganic film exists on/within a polymer.

KEYWORDS Zeolite membrane, Faujasite, Elastic modulus, Atomic force microscopy, PFQNM

1. Introduction:

Zeolites are a family of porous inorganic aluminosilicate materials[1]. Their well-defined pores of molecular dimensions, thermal stability, as well as their ion-exchange properties make them suitable for separations, catalysis, environmental and medical applications[1].

Zeolites can also be fabricated as membranes, and are studied for gas separation and pervaporation[2], with the latter being a commercial process[3]. The separation mechanism of zeolite membranes is distinct from polymer membranes, and in principle, zeolite membranes can have significantly better performance[4, 5]. Self –standing zeolite membranes are fragile[6], so typically such membranes are grown on top of solid supports, alumina being quite common[2]. Zeolite membranes are orders of magnitude more expensive than polymer membranes, primarily due to expensive support materials, batch fabrication process, and the synthesis method leads to defective membranes[2, 7].

Combination of zeolites with polymers is attractive, if the potential for adapting polymer membrane production is feasible, especially if the zeolite membrane synthesis can be speeded up. Several strategies exist for zeolite polymer composite membranes. Mixed matrix membranes are made by a dispersion of zeolite particles within a polymer matrix, and have been studied for gas separations[8]. Another strategy has been to put a very thin layer of nanozeolites on a porous polymer support, followed by the deposition of the gas separation active polymer layer on top of the zeolite film[9]. The transport properties are improved with the zeolite, since the active polymer film thickness can be reduced due to the smooth zeolite film. These composite membranes can be prepared by polymer membrane fabrication methods.

We have reported a method to grow continuous zeolite membranes on top (Type I) of and within (Type II) porous polymer supports[10, 11]. Separation measurements of CO₂ and N₂ by the zeolite-on-top Type I membranes exhibited a large variation in permeance and selectivity, while the zeolite-within-polymer Type II membranes exhibited more reproducible performance. We have hypothesized that the differences in the two membranes stemmed from their different mechanical properties [10, 11]. The concept of forming zeolite membranes on top of alumina supports is the norm (similar to Type I), but there have been few studies of growth of zeolites within the alumina pores (similar to Type II), the latter usually with poorer performance[12, 13].

Unlike the alumina-based zeolite membranes, the zeolite-polymer membranes are flexible, and their mechanical properties are dependent on their elastic constants. Methods to measure elastic modulus of zeolites includes mechanical techniques, such as nano-indentation, micro-deformation, three point bending, and spectroscopic methods such as Brillouin scattering[14-20]. Atomic Force Microscopy (AFM), besides providing high resolution topographic image can also via force-volume (F-V) analysis provide information about the mechanical property of a sample[21]. In Peak Force Tapping (PFT) mode of scanning, the tip is brought intermittently in contact (tapping) with the sample surface while maintaining an amplitude of 100-300 nm. The intermittent contact is modulated with a sinusoidal wave at a frequency of 2 kHz, with amplitude defined by the peak force. In Peak Force Quantitative Nanomechanical Measurement (PFQNM) technique, the individual force curves obtained during PFT scan can be analyzed for mechanical properties, including adhesion, deformation, elastic modulus[22, 23]. PFQNM technique has been used for measuring the mechanical property of a range of materials including polymers[24], ceramic[25], composites[25, 26], biomolecules[27, 28] and cells[29].

In the current work, we have studied the elastic property of Type I and Type II zeolite/polyethersulfone (PES) composite membranes using PFQNM, with the goal of correlating the CO₂/ N₂ separation performance with the mechanical properties of the membranes. To the best of our knowledge, this is the first time this technique is being used for zeolite membranes. In particular, we attempt to understand how the different architecture of the two designs (zeolite layer on top Type I, versus zeolite layer within PES Type II) respond differently to external stress, as measured by the separation performance of these membranes. The practical fabrication process, handling and application of such membranes either in a flat geometry or as spiral wound modules is going to depend on their mechanical properties. The PFQNM technique can also be used in characterizing mechanical property of mixed matrix membranes[8], low dielectric zeolite films [20], hollow fiber membranes[30], and other inorganic-polymer composites, especially where there is a strong mismatch in the elastic constants between the inorganic and organic phases.

2. Experimental Section

2.1 Chemicals:

Aluminum isopropoxide (Al(O-CH(CH₃)₂)₃, 98%), Ludox HS-30 colloidal silica (SiO₂, 30%) and tetramethylammonium bromide ((CH₃)₄NBr, 98%) were purchased from Aldrich (Milwaukee, WI, USA). Tetramethylammonium hydroxide ((CH₃)₄NOH, 25% aqueous) was bought from SACHEM Inc. Sodium hydroxide (NaOH, 99%) pellet was purchased from Fisher Scientific. All chemicals were used without purification. Pure water was produced by a Millipore ultrapure water system.

2.2 Nanozeolite synthesis:

Colloidal nanozeolite particles were prepared according to the literature [10,11,31]. Composition of nanozeolite Y was: 0.048 Na₂O: 2.40 (TMA)₂O(2OH): 1.2 (TMA)₂O(2Br): 4.35 SiO₂: 1.0 Al₂O₃: 249 H₂O, where TMA⁺ is tetramethylammonium cations. Silicon and aluminum sources were prepared separately. For silicon source, 26.2 g Ludox HS-30 was mixed with 10.46 g TMAOH and sealed in bottle with stirring at room temperature. The aluminum source, 12.5 g aluminum isopropoxide was dissolved in mixture of 76.5 g H₂O and 52.3 g TMAOH solution by heating in a water bath at 70 °C. After complete dissolution of aluminum isopropoxide, aluminum source was cooled to room temperature and 13.1 g TMABr was added. The silicon and aluminum sources were mixed. The clear solution was aged at room temperature for 3 days before oil bath heating at 100 °C for 4 days. In product mixture, nanozeolite particles were captured with ultracentrifuge (SorvallTM MX) and washed with distilled water until pH 7.

2.3 Nanozeolite seeding of PES support:

Colloidal nanozeolite dispersion was diluted to specific concentrations. Type I and II membranes were grown from PES support coated with 900 µg/mL and 10 µg/mL nanozeolite dispersions. The polyethersulfone ultrafiltration membrane with molecular weight cut-off of 300 kDa (Biomax PES) was purchased from EMD Millipore Corporation (Billerica, MA). The Biomax PES support has porosity of 15% and mean pore diameter of 70 nm[11]. The porous PES polymer (thickness ~100 µm) is attached on top of a polyolefin non-woven fabric (thickness ~200 µm). As purchased PES 300kDa supports were soaked in water overnight, in isopropanol for 1 hour and back in water for 1 hour before use. In dip-coating process, PES support surface was soaked in nanozeolite seed dispersion for 3 seconds while a vacuum (18 in Hg) was pulled at the back of membrane. As reported in previous studies, PES supports coated with 900 µg/mL and 10 µg/mL nanozeolite dispersions have continuous close-packed

nanozeolite layer on the top of PES and particles within the PES, respectively[10, 11]. After coating, the support was dried at room temperature overnight and stored in plastic sample bags.

2.4 Zeolite membrane fabrication:

Both type I and II zeolite membranes in this study were synthesized according to previously developed method[10, 11]. Briefly, zeolite synthesis gel with composition of 8.3 Na₂O: 1 Al₂O₃: 6.4 SiO₂: 483.9 H₂O was prepared by mixing 2.208 g of Al(OH)₃ and 7.29 g NaOH in 85.24 g H₂O, followed by addition of 13.85 g Ludox SM-30. After 4 hours of aging, gel was transferred to a reaction apparatus with round bottom flask connected with constant-pressure funnel and condenser. In 1 hour of heating, 40 ml of water was evaporated (out of 180 ml) from gel and collected in funnel. Nanozeolite coated PES support was inserted into the concentrated gel before adding water back in another hour. Type I and II zeolite membranes have zeolite layer on top of and within PES supports, respectively [10, 11]. Grown zeolite membrane was washed with water, dried and spin coated with 2 wt% polydimethylsiloxane (PDMS). Polydimethylsiloxane (PDMS) was provided by Wacker Silicones, Inc (Dehesive 944). PDMS solution was prepared by dilution of 35% PDMS stock solution to 2%, followed by addition of cross linker and catalyst with the ratio of 100:1:0.5 (PDMS: Cross linker: Catalyst). Freshly prepared PDMS solution was deposited on zeolite membranes by spin coating, followed by curing at room temperature overnight.

PDMS coated zeolite membranes were crosslinked at room temperature overnight before separation experiments.

2.5 Transport measurements:

Gas separation performance of zeolite membranes were carried out using feed gas of 20% (v/v) CO₂ and 80% (v/v) N₂ with flow rate of 60 mL/min at room temperature. Pure He gas of 30

mL/min was used as sweep gas. Both feed gas and sweep gas were at 1 atm pressure. Gas compositions were studied with gas chromatography using HaySep D column and TCD detector. To initiate failure of the membrane towards gas transport, the membranes were gently bent around columns of different diameters within a few seconds, followed by 200-300 nm PDMS coating and subsequent CO₂/N₂ transport measurements. There was no specific outgassing step, but the membranes were “dried” by passing CO₂/N₂ for at least two hours, until the permeance of the gases reached a steady state, and these are the numbers reported in the paper.

2.6 Characteristics:

Bruker D8 X-Ray Diffractometer with CuK α ($\lambda = 1.5405 \text{ \AA}$) was employed to characterize the phase composition of zeolite membranes. FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) was used to characterize surface morphology of zeolite membrane samples.

2.7 Atomic force microscopy; PFQNM Experiments:

AFM measurements were performed using a Nanoscope V Icon Dimension atomic force microscope (Bruker AXS Corp., Santa Barbara, CA). Images were acquired with peak force tapping mode (Peak Force-Quantitative Nano-Mechanics PF-QNM). Figure A1 shows a model F-D curve in a PFQNM scan, along with the fitting of the F-D curve in order to obtain the elastic modulus). Polymer support, seeded polymer support and grown membrane samples are carefully cut with scissors into 1mm x 1mm section and attached to a disk-shaped steel sample puck with a double faced adhesive and the mounted sample was transferred into AFM chamber. 3mm x 3mm section of a zeolite membrane grown on γ -Al₂O₃ support is cut with a knife. The sample is attached on a steel ample puck with a double faced adhesive like the other samples. The scanning was performed over an area of 5 μm x 5 μm .

The reported value of reduced modulus as obtained from the Bruker Nanoscope Analysis® is accurate only when the Derjaguin-Muller-Toporov (DMT) model holds [22] (equations used for deriving the elastic modulus is presented in the Supplementary Section).

DMT model assumes the tip is infinitely harder than the elastic surface under scanner. Therefore, for accurate data on elastic modulus of a surface, one has to choose probes which have sufficiently high stiffness constant as compared to the scanning surface. We have used three types of AFM probes with different stiffness constants. The stiffness constant and the mass of the tip also controls the natural frequency of the probe. During scanning, the probes are oscillated at a frequency close to their natural frequency. Table A1 (Supplementary Information) summarizes the properties for each probe type used. The selection of the probes for each sample was based on the sample elastic modulus.

The RTESPA silicon cantilevers (supplier spec: 20-80 N/m, 200-400 kHz) are used for scanning PES that is uncoated and lightly coated with nanozeolites. RTESPA-TAP525 silicon cantilevers (supplier spec: 100-400 N/m, 375-675 kHz) are used for scanning heavily PES support coated with high concentrations of nanozeolite and the Type II membrane. Both the cantilevers have aluminum reflective coating on the backside. DNISP-HS diamond cantilever (supplier spec: 300 N/m, 40 kHz) is used for scanning the surface of Type I membrane and the zeolite membrane on alumina support. All scans are performed at a resolution 512 samples/line and rate 0.977 Hz. Data processing was performed using commercial Nanoscope Analysis software (Bruker AXS Corp., Sanata Barbara, CA).

2.8 Calibration:

The quantitative accuracy of the mechanical properties predicted by PFQNM technique depends on acquisition of accurate F-d (Force-displacement) data [22, 25]. Before each

measurement, the probe in use is calibrated using a standard procedure as prescribed by the tip manufacturer. For RTESPA and RTESPA-TAP525, cantilever spring constant and deflection sensitivity was calibrated before each measurement. The DNISP-HS probe is used as-calibrated from the factory. First, the tip qualification calibration was performed by using a ‘tip evaluation’ sample made of polycrystalline titanium coating. The tip qualification routine marks the tip as “SUSPECT”, “GOOD” or “BAD”, based on the preexisting database for each of these conditions. We proceeded with the measurement only when the tip is certified as “GOOD”.

In F-d measurements, the measured cantilever's deflection D contains the information about the applied force F and sample deformation ($d-d_0$) as well. Both of these information are important to the calculation of mechanical properties. For obtaining the individual values of each component, the response of the cantilever on an infinitely stiff surface (i.e. so-called deflection sensitivity, S in [nm/V]) has to be determined. Sapphire sample served as an approximation to the infinitely stiff sample on which the deflection sensitivity was calibrated. Finally, the cantilever spring constant was calibrated by the “thermal tune” routine. In this process, the cantilever is made to vibrate at a range of frequencies and the amplitude peaks at the natural frequency (resonance). A Gaussian peak shows up at the resonant frequency. By fitting the Gaussian peak at resonant frequency, the force constant (k) is calibrated for each type of probe. Once the deflection sensitivity and force constant is known, the applied force F and the tip position d can be calculated as follows:

$$F = kS \quad (1a)$$

$$d = z - SD \quad (1b)$$

where D denotes the cantilever deflection (measured in Volts), z is the vertical scanner position and k is the cantilever spring constant

3. Results

3.1 Membrane synthesis and characteristics

The synthesis and characterization of membranes has been described previously[10, 11]. For the sake of completeness, we summarize these studies. Figure 1 contrasts the synthesis of Type I and Type II membranes.

Figure 1. Schematic description of the synthesis and structure of Type I and Type II membranes.

The main difference is the amount of seeding of the PES layers. For Type I, the seeding level is higher, covering the top surface of PES, whereas for Type II, seeding is primarily done within the pores of PES. The zeolite nanoseeds were prepared in the presence of tetramethylammonium (TMA) ion, and contained TMA both in the sodalite and supercages, the TMA in the supercages was removed by Na^+ ion exchange prior to seed deposition. The zeolite synthesis gel in which the membrane was prepared did not contain any TMA, and it is expected that any TMA ions in the supercage of the seed crystals would be replaced readily by Na^+ ions present in the gel [31]. The amount of seeds used was very little (900 $\mu\text{g/ml}$ for Type I and 10 $\mu\text{g/ml}$ for Type II), and the overall membrane derives its nutrients from the sodium aluminosilicate gel, which does not contain any TMA. So, the growing membrane is expected not to have any TMA. Figure 2 shows the SEM of the top view of the initial PES membrane (Figure 2a), Type I (Figure 2b) and Type II (Figure 2c) membrane. It is clear that Type I has a layer on the top of PES, since the PES pores are no longer visible, and with Type II, there are some isolated zeolite deposits on the PES. Figure A2 shows the X-ray diffraction of the three samples, and it is evident that in Type I and Type II membranes, a faujasitic zeolite layer is formed. When the PES in the Type II membrane is dissolved with N-methyl pyrrolidone, (NMP), an interconnected layer of zeolite is visible in SEM in Figure 2d. The thickness of the zeolite layer in the Type I and Type II membranes are also quite distinct, ~ 250 nm in Type I and 2-3 μm in Type II (also shown as side view SEM in the Supplementary Section in Figure A3).

Figure 2. SEM image of a) PES b) top surface of type I membrane c) top surface of type II membrane d) top surface of type II membrane after dissolution of PES.

3.2 Transport properties of zeolite/PES membranes:

The CO₂/N₂ transport properties of Type I and II membranes were examined. Prior to transport measurements, the membranes were covered with a ~200-300 nm layer of PDMS. Without the PDMS layer, even the membranes that were not subjected to any stress exhibited poor CO₂/N₂ selectivity[10, 11]. We have proposed that as-synthesized membranes have microdefects that are sealed by the PDMS. Both the membranes have good CO₂ separation property, as synthesized (Table 1). Type I membrane had a CO₂ permeance of 789 GPU, N₂ permeance of 10 GPU, and CO₂/N₂ selectivity of 72.3, whereas Type II membrane had CO₂ permeance of 1296 GPU, N₂ permeance of 28 GPU, and CO₂/N₂ selectivity of 46.1.

Mechanical stress was applied by bending the two membranes around a certain curvature (Figure A4 shows schematic of the bending process). The transport properties were measured after bending, and Table 2 summarizes the transport data. Type I membranes fail to separate CO₂ from binary CO₂/N₂ gas stream (selectivity 1-2) after bending at a radius of curvature of 2 inches. Type II membranes maintains the CO₂ permeance (1300-1800 GPU and CO₂/N₂ selectivity (>40) until bending in the convex (or concave) direction up to a radius of curvature 1 inch (Table 2), and the CO₂/N₂ selectivity disappears (3-4) once the bending radius is reduced to

0.5 inch (Table 2). Thus type II membrane can withstand a higher degree of tensile and compressive strain. We have shown that this flexibility of Type II membrane can have practical implications, since we could use a roll to roll type process for their fabrication[32]. How the elastic properties of these membranes determine the behavior just discussed is of interest.

3.3 Validity of PFQNM experiments for estimating elastic constants:

Since the mechanical properties of silicon are well known, it was used as a model system, [33]. Figure A5 shows the topographic image, height map, elastic modulus map, and the reduced elastic modulus profile along a typical line section. The average reduced elastic modulus of the scanned surface is 180 GPa with a standard deviation of 20%. The reported Young's modulus of Si wafer is in the range of 130 -188 GPa , with a range of Poisson's ratio 0.040-0.48[33]. The Poisson's ratio (ν) of most materials vary between 0.2 (perfectly incompressible) and 0.5 (perfectly plastic). It is a common practice to report the reduced elastic modulus measured by PFQNM, if the Poisson's ratio is unknown [22]. The difference between the reduced and actual elastic modulus can be at most 25%, depending on Poisson's ratio. Unless explicitly mentioned, work we use the reduced elastic modulus. The observed elastic modulus value for silicon is in agreement with literature reports, and supports the validity of the approach.

3.4 Analysis of PES and seeded PES:

3.4.1 Topographic Characteristics

3.4.1.1 PES

Figure 3a shows the topographic image of the bare polyethersulfone (PES) support, the dark spots mark the pores on the PES surface. The height profile (Z vs lateral distance) indicates the pore locations, and from their width, the dimensions of pore openings can be estimated [34,35].

Figure 3. a) Topographic image and the height vs distance plot for a) PES, b) high seeded zeolite PES and c) low seeded zeolite PES.

A range of diameters of the pore opening from 120 nm to 1.3 μm is observed. The pores with the largest opening have a height difference of ~125 nm from the highest to the lowest point. We can assume this as the limit of the depth the tip is able to analyze, and will be relevant when zeolite particles are deposited in the pores.

3.4.1.2 High zeolite seeded PES

Figure 3b shows the topographic image and height profile of a high seed loading (solution used for seed loading has 900 μg/ml 40 nm nanozeolite for Type I membrane) coated PES surface. No exposed pore openings are visible in the topographic image (the dark spots come from height differences due to depressed areas of the polymer). The average surface roughness (R_a) is 9 nm.

Low roughness as compared to PES points to the close packing of zeolite nanoparticles on the surface.

3.4.1.3 Low zeolite seeded PES

Figure 3c shows the topographic image and height profile of low seeded nanozeolite (solution used for seed loading has 10 $\mu\text{g/ml}$ of 40 nm nanozeolite for Type II membrane) coated on PES surface. The surface does not have a uniform close packed coating of nanoparticles, and exposed pores are visible in the topographic feature. This is consistent with the low concentration of nanozeolite used for vacuum dip coating, as is also evident in the SEM picture shown in Figure A6, where only a few crystals are visible on the surface, and mostly within the pores. The dip in the height at pore regions are < 70 nm which points to the fact that the tip encounters solid surface at this point (with bare PES this distance was 120 nm, Figure 3a), indicating the presence of nanoparticles inside the pores. The surface roughness is ~ 16 nm and is controlled by two factors. In absence of a continuous layer of nanoparticle the tip senses the exposed pores of PES support making the surface rougher. On the other hand, presence of nanoparticle inside the pores decreases the depth of the pores.

3.4.2 Elastic Modulus Characteristics

3.4.2.1 PES

Figure 4a is a map of the elastic modulus of PES. The average reduced elastic modulus of the area is 2.1 GPa with standard deviation 0.7 GPa. For PES, the Poisson's ratio is reported as 0.35[36], and the calculated elastic modulus of 1.9 GPa is within the standard deviation of earlier reported value of 2.5 GPa for PES. The elastic modulus suffers a dip inside the pores, and is due to increased adhesion within a pore[37].

Figure 4. Map of reduced elastic modulus and reduced modulus vs distance plot for a) PES, b) high seeded zeolite PES and c) low seeded zeolite PES.

3.4.2.2 High zeolite seeded PES

Figure 4b is the elastic modulus map of high zeolite seeded PES, with an average reduced elastic modulus of 12.3 GPa with a standard deviation of 1.8 GPa. Poisson's ratio of zeolite materials is in the range of 0.20 -0.45[16, 19, 38, 39]. The reported elastic constant of FAU type NaX zeolite (being used in the present study) is in the range of 38-41 GPa[39, 40]. Both the height map (Figure 3b) and the modulus map (Figure 4b) shows cracking of the top surface, due to evaporative drying of nanoparticle dispersion coating the polymer support [41]. The nanozeolite coating on PES increased the elastic modulus from 2.1 to 12.3 GPa, similar to observations of nanozeolite films on porous organosilicate glass [19].

3.4.2.3 Low zeolite seeded PES

Figure 4c shows the modulus map of a low zeolite seeded PES, with an average reduced elastic modulus of 3.6 GPa with a standard deviation of 0.5 GPa. The elastic modulus is consistently higher than the bare PES by almost ~ 1.5 GPa, due to the presence of the nanozeolite particles beneath the top surface. Nanosilica dispersed in polyethylene has been reported to lead to an increase in elastic modulus [42].

3.5 Analysis of zeolite membranes/PES

3.5.1 Type I membrane

Figure 5a shows the topographic image and height profile of a Type I membrane grown from the highly seeded zeolite system. The topographic image shows the growth of a continuous polycrystalline layer of zeolite, also supported by the top view SEM shown in Figure 2b. The average roughness (R_a) over the whole area is ~ 40 nm. The height profile shows that the difference between the peak and the trough is ~ 200 nm and is constituted by different sized zeolite grains growing on the polymer support.

Figure 5. a) Topographic image, and the height vs distance plot on the marked line section (red)
b) map of reduced elastic modulus, and reduced modulus vs distance plot on the marked line section (blue) of a Type I membrane surface

From the modulus map in Figure 5b, the average reduced elastic modulus over the scanned area is measured to be 21.9 GPa, with a standard deviation of 2.2 GPa. In the line section of elastic modulus we always see a dip at the grain boundaries (Figure 5b), due to the increased adhesion forces at the grain boundaries. The peak reduced elastic modulus (~28 GPa) is reached on top of the grains. Subject to the reported value of Poisson's ratio of zeolites (0.2), the peak value of actual elastic modulus (Young's modulus) of zeolite crystals is calculated as ~27 GPa. This is lower than the reported value of the zeolite Young's modulus (38-41 GPa) [39, 40]. Since there is a large elastic mismatch between the zeolite film and the PES substrate, the elastic modulus for the composite is expected to be lower than the zeolite by itself [43]. The average value of the elastic modulus of the composite made by growing a continuous zeolite layer on a harder porous γ -Al₂O₃ support (elastic modulus varies between 150 to 400 GPa [44]) is ~51 GPa, greater than the zeolite, but lower than the support (Figure A7). Thus, the lower stiffness of the seeded as well as the continuous zeolite layer is due to 'substrate factor' arising from the more ductile PES. In summary, the elastic modulus increases from ~12 to ~22 GPa as zeolite seed crystals are transformed to a continuous zeolite layer in Type I membrane. This stiffening upon membrane formation is due to the chemical interconnectivity of the seed crystals in all three dimensions.

3.5.2 Type II membrane\

Figure 6a shows the topographic image and height profile of a Type II membrane grown from a low seeded system.

Figure 6. a) Topographic image and the height vs distance plot on the marked line section (red) and map of reduced elastic modulus and reduced modulus vs distance plot for b) Type II membrane surface c) of a surface obtained after dissolving the PES from a Type II membrane

The pores of the PES support are visible with scattered deposits of zeolite crystals on the top surface, and supported by the SEM shown in Figure 2c (diffraction pattern in Figure A2 indicates the presence of zeolite FAU). The surface has a roughness of 120 nm. This is due to inhomogeneity in terms of height on the top surface (i.e. presence of exposed pores as well as zeolite particles).

From the elastic modulus map in Figure 6b, the average reduced elastic modulus of the scanned area is 10.1 GPa, with a standard deviation of 5.5 GPa. The reason for high standard deviation is the inhomogeneity of the top surface. The line section of the reduced elastic modulus shows that on top of the scattered crystals the value reaches to ~27 GPa, same as the zeolite

grains for Type I membrane. The elastic modulus inside the exposed pores and the edges are in the range of 4-6 GPa, which is consistently higher (by ~1.5 GPa) than the low seeded PES support (Figure 4c).

We dissolved the PES with N-methylpyrrolidone and imaged the inter-grown zeolite film that had formed within the PES pores. Figure A8 shows the topographic image and height profile. The topographic profile of the surface is markedly different from the undissolved Type I membrane surface. The average surface roughness (R_a) is 200 nm, and the distance between peak and trough is ~400 nm (twice of the Type I surface). The reason for this variation is that the interconnecting zeolite layer grows in all three directions through the PES pores, with domains of PES between the adjacent grains.

From the elastic modulus map of the inter-grown zeolite film shown in Figure 6c, the average elastic modulus is 21.2 GPa with a standard deviation of 6.9 GPa, which is similar to the continuous zeolite layer on top of Type 1 membrane (Figure 5b). So elastically, the isolated intergrown zeolite layer behaves as Type I membrane. It is noticeable (Figure 6c), that at some places the elastic constant has the value as low as 2-3 GPa. At these regions, the tip encounters the non-woven fabric. There are regions of the PES-zeolite composite which has no zeolite, dissolving the PES at these areas leaves the non-woven fabric exposed to scanning tip. In summary, though the isolated inter-grown zeolite layer for Type II membrane has elastic modulus (~21 GPa) comparable to the zeolite layer grown on top of PES (Type I, ~22 GPa), the intact Type II membrane before PES dissolution has a considerably reduced elastic modulus of 4-6 GPa.

4. Discussion

Table 1 summarizes the dimensions and elastic property of each layer of the Type I and II membranes. For Type I membrane, the ~250 nm top layer is the continuous zeolite layer on top of the PES, which has an average reduced modulus of 21.9 GPa. The second layer of 250 nm thickness is the nanozeolite seeded layer within the PES, with an average reduced modulus of 12.3 GPa. The next two layers are bare PES layer and non-woven fabric with reduced moduli of 2.1 and 1.9 GPa, respectively[45-47]. For Type II membranes, the top layer is the zeolite layer that has grown inside the 3D interconnecting pores of PES, with an average reduced modulus of 5.0 GPa with a standard deviation of 1.5 GPa.

In any films subjected to a bending stress, there is a layer that does not undergo a change in dimension, and is referred to as the neutral layer (see Figure A4). For structures with variable elastic constant and thickness, Hu *et al.*[48] have proposed an equation to calculate the shift in neutral layer in the structure. For such n-layered system, on bending the neutral layer shifts from the central position to the higher elasticity region by a magnitude of

$$z^*(\epsilon = 0) = \sum_{i=1}^n E_i^* d_i \left[\left(\sum_{j=1}^i d_j \right) - d_i/2 \right] / \sum_{i=1}^n E_i^* d_i \quad (2)$$

where E_i^* , and d_i 's are reduced elastic modulus and thickness of i 'th layer. In this equation top layer $i=1$ layer is assumed to be bent in convex direction. Using Equation (2) and the modulus and layer thickness data, the depth of the neutral layer was calculated to be 144.02 μm for Type I membrane and 144.69 μm for Type II membrane (calculated from the top of the membrane). Since the zeolite layer is in the top few microns of both membranes, the shift in the neutral layer

between the two membranes is not consequential (we have made the approximation that the measured modulus corresponds to the modulus of the layers, considering that the PES and non-woven fabric are much thicker than the zeolite layer, this is a valid approximation).

However, knowing the position of neutral layer, the strain on bending at the top surface can be calculated from the equation (3),

$$\epsilon^* = \frac{z^*}{\rho} \quad (3)$$

where z is the distance of the top surface from neutral layer and ρ is the radius of curvature (Figure A4). From the transport data shown in Table 1 with bending, we notice that Type I membranes fail at 2 inch curvature, if the membrane was intact this level of bending corresponds to a 0.28% (0.30%) tensile (compressive) strain (all strains are shown in Table A2). Type II membrane fails at a 0.5 inch curvature, which corresponds to a tensile strain of 1.14% (1.21% for compressive strain). So Type I will fail between the strain levels 0-0.28% and the Type II will fail between the strain levels 0.6-1.2%. Thus, Type II membranes can tolerate higher amounts of compressive strain. The problem in reproducibility of transport properties observed with Type I membrane stems from this fact, even the strain generated in handling can disrupt the membrane [10]. Silicalite zeolite layer grown on top of metaglass have been shown to withstand a strain of 1.62% [49] .

Using the values of 2.1 GPa measured for PES, and 39.5 GPa for zeolite alone (as reported by Baimpos *et al.*[40], this value is free from substrate effects), and assuming that 15% of the volume fraction of the PES is porous and occupied by the zeolite, the elastic modulus of the composite calculates to a Voigt upper limit of 7.7 GPa, as compared to the experimental observation of 5.0 ± 1.5 GPa. Since the elastic modulus of the composite layer (zeolite-PES) is

close to the Voigt limit, which assumes an isostrain scenario for the composite, this suggests that both the components, PES and zeolite undergo same level of strain. So it is surprising why the zeolite layer in Type I fails at strain of 0.28% , whereas with the zeolite in Type II, the transport property is still intact at 0.61% strain[Table A2]. To explain, we propose a qualitative model for membrane failure mechanism based on the PFQNM data and SEM image of membranes post bending.

Figure 7. SEM of crack propagation in a) Type I and b) Type II membranes

Figure 7 shows the electron micrographs of the membranes after they are subjected to strains that result in total loss of transport performance. There are cracks visible in the membranes. For Type I membrane, the crack propagates in a vertical direction through the zeolite layer and into the PES. For Type II membrane, the crack bends through the PES layer. For Type I membrane, the crack length exceeds the 250 nm zeolite layer thickness, and the released stress is enough to rip the PES apart. For Type II membranes, the zeolite layer is within the PES pores. Thus, cracking can be initiated only at the brittle zeolite domain of the composite, and the maximum dimension of these cracks can be ~75 nm (mean dimension of pores in PES). We propose that the energetics of the smaller cracks in Type II ensures that the PES interface can arrest these cracks, unlike the cracks in Type I . The concept of an interlayer arresting a microcrack is well known. Organic adhesives can arrest cracks in a brittle material such as glass[50], and

microcracks in bone can be arrested at the cement organic layer[51, 52]. The smaller sized cracks formed in zeolite domains in Type II membranes upon bending are still able to provide desired CO_2/N_2 selectivity after the PDMS cover[53], until the crack grows covering the adjacent pores. In order for this to happen, microcracks in neighboring zeolite domains will have to connect, and this leads to the curvilinear cracks seen in Figure 7b. Figure 8 shows a schematic representation of the crack propagation process. Type I membranes exhibit the straight crack through the cross section (Figure 8a). For Type II, the initial cracks are within the pores, arrested by the PES (Figure 8b), and can be sealed by PDMS. With tighter bending, adjoining cracks can join (Figure 8c), leading to catastrophic failure. Interestingly, many decades ago it was shown that polysulfone is an effective bone implant material with the bone growing within the pores, resulting in high interfacial shear strength for the composite[54].

Figure 8. Schematic of a cross section of a) a cracked Type I membrane and b-c) cracked Type II membrane

The cracking of zeolite membranes grown on rigid supports has been extensively studied, and there are some parallels to our present observations [55-62]. Drying of a membrane can cause cracks, e.g. for FAU, a strong expansion of the unit cell was noted on heating from 50 to 450°C [59]. Since all our experiments were carried out with membranes that were dried at room temperature, the influence of drying on crack formation is not expected to be significant. Zeolite Y grown on a Cu substrate exhibited cracking at the zeolite-metal interface, due to poor adhesion [55]. Cracks that are generated at the support-zeolite boundary due to thermal mismatch are quite distinct from what we are observing with application of mechanical stress to the polymer support. Cracking is commonly observed after calcination at high temperatures to remove structure-directing agents, and extensively studied for MFI membranes, including those architectures that exhibit specific orientation of crystals [57]. With supports that can form chemical bonds during calcination with the zeolite (e.g. yttria doped zirconia), compressive forces are generated upon cooling down, and can result in cracks [56]. With alumina supports, where a bond between the support and crystal is formed during synthesis, the removal of the organic during calcination will diminish the size of the zeolite grains, resulting in tensile stress [56]. For MFI membranes, where the membrane grows into the support [58], as with the Type I membrane (Figure 8a), tensile stress can cause cracks that propagate vertically through the support, as observed in Figure 7a. Using porous zeolites as supports can minimize cracking arising from thermal mismatch [60]. Rapid thermal processing can eliminate grain boundary defects [61]. Vapor phase transport synthesis of mordenite membranes also can minimize defects [62]. The concept of using the polymer support to arrest cracks as we propose with Type II membranes (Figure 8b) has not been noted with zeolites on inorganic supports.

Measurements of elastic modulus of zeolite-polymer composites also opens up several interesting avenues of research. For aluminosilicate geopolymers, it has been shown that the modulus depends on the Si/Al ratio, as well as the nature of the charge-balancing cation [63]. Therefore, mechanical properties of high Si/Al FAU [64], as well as other frameworks, such as chabazite [65] coupled with polymer supports should be of interest.

5. Conclusions

Continuous zeolite membranes on top (Type I) of and within (Type II) porous polyethersulfone polymer supports are investigated. Separation measurements of CO₂ and N₂ by the zeolite-on-top Type I membranes exhibited failure upon bending around a radius of curvature of 2 inch, whereas the zeolite-within-polymer Type II membranes exhibited failure upon bending with a radius of curvature of 0.5 inch. Peak Force Quantitative Nanomechanical Measurement (PFQNM) technique using Atomic Force Microscopy has provided values of the reduced elastic modulus of Type I and II membranes. These data show that Type I membranes have a modulus of 21.9 GPa, whereas Type II membranes have a modulus of 5.0 GPa. The higher ductility of the Type II membrane allows it more flexibility. We propose that cracks in the zeolite occur with both Type I and Type II membranes, but that in Type II membranes, the cracks are arrested by the polymer, giving it more flexibility. Thus, Type I membranes fail at $> 0.28\%$ strain, whereas Type II membrane fails at a strain $> 1.14\%$.

Appendix A. Supplementary Material

The material contains details of neutral layer and strain calculation schemes, description of elastic modulus and roughness calculation in Nanoscope® software from PFQNM data, tables with the summary of the mechanical properties of AFM probes and calculated strains on

different layers on type I and type II membranes, sample demonstration of force-displacement data and its processing in PFQNM technique, XRD and cross section SEM of the two membrane types and schematic of the failure analysis test by bending for the two membrane types.

Author Contributions

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TABLES

Table 1. Summary of the mechanical property and dimension of each layer of type I and type II membrane and the separation performance of the two membranes in unstrained, as-prepared condition

Membrane Type	Layers	Thickness	Reduced modulus	CO ₂ separation performance
Type I	Crystalline zeolite layer	250 nm	21.9(±2.2) GPa	CO ₂ Permeance = 789 GPU, N ₂ permeance = 10 GPU, CO ₂ /N ₂ selectivity = 72.3
	Nanozeolite seed layer	250 nm	12.3(±1.8) GPa	
	PES support	100 µm	2.1(±0.7) GPa	
	Non –woven fabric	200 µm	1.8 GPa*	
Type II	Zeolite-PES composite layer	2 µm	5.0(±1.5) GPa	CO ₂ Permeance

	PES support	98 μm	2.1(± 0.7) GPa	=1296 GPU, N ₂ permeance =28 GPU, CO ₂ /N ₂ selectivity = 46.1
	Non –woven fabric	200 μm	1.8 GPa *	

* The reduced elastic modulus is calculated from reported Young's modulus and Poisson's ratio using Eq. 4(Supplementary Section)

Table 2. Transport properties of Type I and Type II membranes as a function of curvature

Sample	Bending Radius of Curvature	CO ₂ Permeance /GPU	N ₂ Permeance /GPU	CO ₂ /N ₂ Selectivity
Type II	Straight	1296.6	28.1	46.1
	1 inch Convex	1461.9	35.5	41.2
	1 inch Concave	1843.2	42.3	43.6
	0.5 inch Convex	475.7	101.8	4.7
	0.5 inch Concave	645.0	191.4	3.4
Type I	Straight	789.0	10.9	72.3
	2 inch Concave	393.7	245.2	1.6
	2 inch Convex	468.6	322.7	1.5

Continuous Zeolite Membrane

On top of polymer support

Elastic modulus: 27 GPa

Bendable Zeolite Membrane

Within polymer support

Elastic modulus: 5 GPa