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## Tolerance of polymer-zeolite composite membranes to mechanical strain

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## 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 CO<sub>2</sub>/N<sub>2</sub> 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.

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## 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

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supports [10,11]. Separation measurements of CO<sub>2</sub> and N<sub>2</sub> 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 CO<sub>2</sub>/N<sub>2</sub> 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(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, 98%), Ludox HS-30 colloidal silica (SiO<sub>2</sub>, 30%) and tetramethylammonium bromide ((CH<sub>3</sub>)<sub>4</sub>NBr, 98%) were purchased from Aldrich (Milwaukee, WI, USA). Tetramethylammonium hydroxide ((CH<sub>3</sub>)<sub>4</sub>NOH, 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 Na<sub>2</sub>O: 2.40 (TMA)<sub>2</sub>O(2OH): 1.2 (TMA)<sub>2</sub>O(2Br): 4.35 SiO<sub>2</sub>: 1.0 Al<sub>2</sub>O<sub>3</sub>: 249H<sub>2</sub>O, where TMA<sup>+</sup> 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 H<sub>2</sub>O 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 (Sorvall™ 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 300 kDa supports were soaked in water overnight, in isopropanol for 1 h and back in water for 1 h before use. In dip-coating process, PES support surface was soaked in nanozeolite seed dispersion for 3 s 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 Na<sub>2</sub>O: 1 Al<sub>2</sub>O<sub>3</sub>: 6.4 SiO<sub>2</sub>: 483 · 9H<sub>2</sub>O was prepared by mixing 2.208 g of Al(OH)<sub>3</sub> and 7.29 g NaOH in 85.24 g H<sub>2</sub>O, followed by addition of 13.85 g Ludox SM-30. After 4 h of aging, gel was transferred to a reaction apparatus with round bottom flask connected with constant-pressure funnel and condenser. In 1 h 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.

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