

# Quantifying the Transport Properties of Thin Polymer Gels via an Indentation-Based Technique\*

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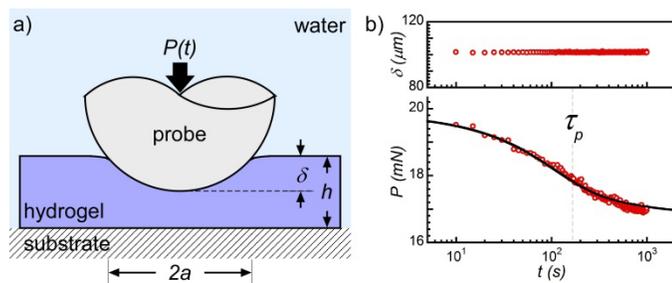
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## INTRODUCTION

Thin swollen polymer network layers are prevalent in many technological applications including membranes for water purification, proton exchange membranes in fuel cells, as well as scaffolds for tissue engineering and drug delivery vehicles.<sup>1</sup> In these examples, their performance is closely linked to the ability to control transport of small molecules such as solvent. Understanding the critical time- and length-scales that regulate transport of these molecules within the polymer network will enable development of membrane materials with the desired performance.

Recently, an indentation approach has been demonstrated to quantify the poroelastic relaxations of hydrogels.<sup>2</sup> This approach is attractive for measuring the material properties of swollen polymer networks for two reasons. First, the approach is quite simple and straightforward since it only involves compressing the material at a fixed displacement with a macroscopic spherical probe (Fig. 1a). Therefore, the test facilitates direct measurements of the properties of a film that is supported by a substrate. Second, the approach can measure several material properties including diffusion coefficient, shear modulus, and average pore dimensions with a single test.<sup>3</sup> We can envision utilizing this approach for polymer membranes as the poroelastic response can be directly correlated to the material properties such as diffusion coefficient and average pore size.

Although the approach has been demonstrated to quantify the transport properties of thick hydrogel materials, its relevance for thin hydrogel layers and other hydrated polymer membranes have yet to be explored. In this work, we demonstrate POraelastic Spherical Indentation Testing (POSIT) in quantifying the transport properties for model thin swollen polymer network based on poly(ethylene glycol) (PEG) hydrogel layers.



**Figure 1.** a) Poroelastic relaxation measurement by the POraelastic Spherical Indentation Testing (POSIT) approach. b) Representative results of the testing approach. The test is based on stress relaxation, where a fixed compressive displacement ( $\delta$ ) is applied to deform the hydrogel. This deformation results in the relaxation of the compressive force ( $P$ ). The time-scale of this relaxation process is defined as the poroelastic relaxation time ( $\tau_p$ ) and is associated with the transport of water from the region of material under contact ( $\sim a^2$ ) to the surrounding water region.

## EXPERIMENTAL

Representative results for POSIT is presented in Fig. 1. The approach involves compressing a hydrogel with a rigid glass indenter (probe radius = 5 mm) to a predefined constant displacement value ( $\delta$ ) (Fig. 1a). In response to this constant deformation, the hydrogel will undergo a stress-relaxation process that is time-dependent (Fig. 1b). Since the contact radius ( $a$ ) is on the order of 100  $\mu\text{m}$ , the characteristic relaxation time of the test is indicative of poroelastic relaxation time ( $\tau_p \approx 100$  s). Qualitatively, the test is similar to squeezing water out of a sponge. Specifically, the poroelastic time reflects the amount of time required for the hydrogel to establish a new chemical potential with the pure water environment due to the constant deformation. Thus,  $\tau_p$  is defined as  $a^2/D$ , where  $D$  is the diffusion coefficient of water within the hydrogel.<sup>2,4</sup>

## RESULTS AND DISCUSSION

We first applied the measurement approach to quantify the diffusivity of thick layers of model PEG hydrogel layers. Our results showed excellent agreement between model predictions and reported literature values,<sup>5</sup> which provide confidence in the general applicability of our approach.

To demonstrate the approach for thin membranes, we examined the effect of hydrogel film thickness on the changes in transport properties. Based on our modeling results, geometric confinement due to reduction in film thickness at constant probe radius leads to an enhanced stiffness of the hydrogel because of the mechanical coupling with the stiff substrate backing layer.<sup>6</sup> In general, this enhanced stiffness leads to a decrease in the apparent diffusion coefficient since the density of the crosslinks for the hydrogel network appears to be larger than expected. By correcting for this enhanced stiffness, the POSIT measurements of these thin layers revealed that the diffusion coefficient, as well as other materials properties are similar to that of the thick hydrogels.

## CONCLUSIONS

Our present results provide a quantitative measurement of the transport properties of thin polymer hydrogel layers and offer insight into the effect of geometric confinement on the poroelastic response. We believe that the proposed methodology is practical and applicable to a wide variety of thin membrane materials and devices.

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