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Permeation control in hydrogel-layered patterned PET membranes with defined switchable pore geometry – Experiments and numerical simulation

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ABSTRACT

Permeation through polymeric membranes can be controlled by surface coating of a polyethylene terephthalate (PET) membrane with poly(N-isopropylacrylamide) (PNIPAAm) and inserting pores of defined geometry. When the temperature of the system rises above the volume phase transition temperature, the pores open, which allows permeation of formerly blocked particles. The exact control of the temperature allows defined change of the pore size and therefore enables separation abilities. Free swelling experiments are conducted to obtain the swelling behaviour of PNIPAAm. Then, a temperature expansion model is derived in order to simulate this behaviour with the finite element tool ABAQUS. The gained results are in excellent agreement with the observed shape change. Membranes with permeation control of particles can be used for biomedical application in microfluidics to analyse the size distribution of cells or in chemical information processing as a transistor-like component for an information-bearing chemical species. The possibility to simulate the behaviour of such permeation systems allows computer aided design and prediction of permeation abilities in these areas.

1. Introduction

Membranes are entities to separate compartments of different fluids. In biology, bilayer lipid membranes are self-assembling structures made of amphiphilic phospholipids. Embedded proteins allow specific permeation abilities for ions and molecules, which in some cases can be controlled by physical stimuli including electrical, chemical, mechanical and thermal signals. The underlying process is called gating [1].

In technology, membranes can be made of polymers with different porosity regarding their application area, e.g. filtration or reverse osmosis [2]. The technological equivalent of gating shall be called permeation control henceforth. Besides permeation control of ions and molecules, in life science, membranes for separation of particles with characteristic sizes in the sub-micron to micron range are of interest. Permeation control can be used in medicine to generate particle size profiles, e.g. in blood to analyse cells of anomalous size such as cancer cells. Another application area is the use as chemomechanical valves for flow control [3] or as transistor-like components for microfluidic integrated circuitries with a transistor circuit-based information processing concept [4].

In the present work, membranes with dynamically adjustable pore diameters and therefore tunable separation abilities controlled by temperature are introduced. Experimental results are given and the validity of the mechanical modelling with a temperature expansion model is shown. This allows the computer aided design of the filtration membranes with varying separation abilities.

Various research groups focus on porous polymer membranes made of stimuli responsive gels [5–9], where the permeation control is realised by a change in the hydrogel porosity. Further approaches use nanotubes [10–13] to achieve selective ion transport. The term *switchable gate membrane* [14,15] is also used for membranes which are surface functionalised to hinder transport parallel to the surface direction. Different groups have already used sensitive hydrogels for flow control [3] and as microfluidic valves [16]. Other research groups focus on the incorporation of

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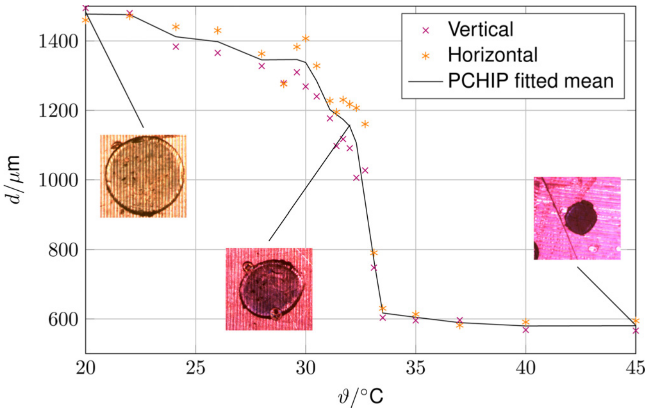

Fig. 1. Diameter of the disc versus temperature of a PNIPAAm sample. The mean value of the measurements is fitted with piecewise cubic Hermite interpolating polynomials (PCHIP).

biological membrane proteins into bilayer lipid membranes to achieve permeation control through natural gating mechanisms [17,18]. In the context of lab-on-a-chip devices, separation can be achieved in constant flow, e.g. by using branching [19] or capillary forces in microfilters [20].

The present work aims at a direct control of the permeation abilities. We demonstrate how permeation control membranes are designed, how the system can be characterised and how the properties of the smart actuator material can be transferred to a model of the experimental setup for numerical analysis. Therefore, the free swelling behaviour of the hydrogel poly(N-isopropylacrylamide) (PNIPAAm) is experimentally obtained (Section 2.1). A temperature expansion model for hydrogel swelling is derived in Section 2.2 and then implemented in a finite element tool to perform simulations. To verify the model, the free swelling behaviour of a simple model test setup is compared to the measured experimental values in this section as well. The design and the experiments of the switchable membrane are depicted in Sections 3.1 and 3.2; its numerical simulation is performed in Section 3.3. Additional information about the pore size evaluation from experimental microscopy results is given in Section 3.4. The results of the comparison between experiment and simulation for the complete permeation control system are depicted in Section 4. The conclusion is drawn in Section 5. Additional information is given in Appendix A.

2. Development of the material model

2.1. Free swelling behaviour of PNIPAAm

PNIPAAm shows lower critical solution temperature (LCST) behaviour. The swelling of the gel occurs due to the attracting chain interactions and the screening effect of water molecules (hydrohpilic interaction). For temperatures lower than LCST, the good screening properties of water molecules lead to a reduced interaction between the PNIPAAm chains, resulting in swelling. Those properties are lost when the temperature and subsequent movement/rotation of the water molecules increases over LCST. Then, there is a stronger attraction between PNIPAAm chains and the volume decreases, i.e. deswelling occurs. The process can be described as a first order volume phase transition [21].

To investigate the real swelling behaviour of the gel, a plate-like pad made of poly(N-isopropylacrylamide) is investigated under different temperatures (Fig. 1). At a temperature of 32 °C, the diameter is 1000 µm and the height is 120 µm. Below a temperature of 29 °C the PNIPAAm is completely swollen. Exceeding this temperature, the hydrogel collapses until it is completely shrunken at 35 °C. The experiments agree with the volume phase transition temperature of PNIPAAm in pure water [22], which is 32.8 °C.

Further information about the modelling background of the free swelling behaviour is given in Appendices A.1 and A.2. Image analysis is performed as described in Section 3.4. The pad diameter vs. temperature data is needed to calibrate the material behaviour with the temperature expansion model explained in Section 2.2.

2.2. Modelling and simulation of the thermal induced swelling of a PNIPAAm sample

The stress-free swelling of a hydrogel is assumed as an isotropic deformation. The underlying processes are given, e.g. by Attaran et al. [23] In the present work, we use a quasi-static temperature expansion model for the thermal swelling behaviour. Dynamic processes like temperature flux and locally varying strains are not taken into consideration in the present work. In contrast to other authors like Trinh et al. [24], our model is not an analogy for the chemical behaviour, but directly depicts the thermal volume expansion of the hydrogel as a linear-elastic material under varying temperature. In other works, the osmotic pressure derived from the ion distribution combined with a temperature dependent coefficient [25] is used to derive the swelling behaviour. The governing equations of the quasi-static thermo-mechanical problem are the mechanical balance equations

$$\sigma_{kl,k} + f_l = 0, \qquad \sigma_{kl} = \sigma_{lk} \tag{1}$$

the kinematics relation

$$\varepsilon_{kl} = \frac{1}{2}(u_{k,l} + u_{l,k}) \tag{2}$$

and the material law

$$\sigma_{kl} = E_{klmn}(\underbrace{\varepsilon_{mn} - \alpha \quad \delta_{mn} \quad \Delta\vartheta}_{\varepsilon^{el}_{mn}}) \tag{3}$$

where σ_{kl} is the stress tensor, f_l the volume load, ε_{kl} the strain tensor and E_{klmn} the tensor of elasticity. Please note that the equations are given in index notation for $k, l, m, n \in [x, y, z]$ and a summation over identical indices is performed (Einstein convention). $()_{,k}$ denotes the derivative in space with respect to the direction x_k. In the present case, there is no volume load, hence $f_l = 0$. The change of volume due to a temperature difference $\Delta\vartheta$ is defined through an isotropic strain with δ_{mn} being the Kronecker-Delta. In order to avoid buckling phenomena and allow superposition of thermal and mechanical strains, we use linear kinematics and the linear theory of elasticity, where the components of the strain tensor ε_{kl} are described via the gradients of the displacement u_k. For large deformations, the deformation gradient must be decomposed multiplicatively [26]. For a discussion about the linear and nonlinear approach, please see Appendix A.2. In the present form, the total strain ε_{kl} is gained by superposition of the thermal strain $\varepsilon^{\text{th}}_{kl}$ and the elastic strain $\varepsilon^{\text{el}}_{kl}$

$$\varepsilon_{kl} = \varepsilon^{\text{th}}_{kl} + \varepsilon^{\text{el}}_{kl} \tag{4}$$

The elastic strain $\varepsilon^{\text{el}}_{kl}$ is gained by the generalised Hooke's law (3) for linear isotropic deformation of a simple material. No viscous effects are considered, because the experiments are conducted in quasi-static condition, i.e. every point on the swelling curve (Fig. 1) is in thermal and chemical equilibrium.

To transform the swelling curve into an equivalent thermal expansion, the pad diameter, which describes the isotropic problem, is used. Preliminary studies on the analytical solution of the disc problem have proven that this approach is valid. Application of the pad area, which is not exactly circular due to manufacturing inaccuracies, instead of the mean diameter have proven to yield