

Nanocomposite membranes inspired by the architecture of plant cuticles

Aristotelis Kamtsikakis

Over the course of time, plants evolved a plethora of mechanisms and structural innovations as survival mechanisms. Among these innovations, plants integrated a thin composite membrane on their vascular tissues: the cuticle, a non-porous composite membrane which functions primarily as a mass transport regulator tuning the diffusion of small molecules such as water. The three primary components of cuticular membranes are polysaccharides, cutin (a fatty acid-based polyester), and non-polar waxes. In most cuticles, these constituents are asymmetrically assembled thus creating a compositionally graded architecture. This structure is typically rich in polar polysaccharides towards the interior, whereas non-polar waxes dominate the exterior portion of the cuticle. As in the case of mass transport through artificial compositionally graded and layered membranes, the transversally graded architecture of plant cuticles could theoretically induce asymmetric transport properties of small molecules through these membranes, which is a feature that has hardly been investigated.

To imitate the complex cuticular architecture, nanocellulose — a renewable nanofiller isolated from the most abundant biopolymer — can be used as a tailorable material to prepare similar compositionally graded structures and provide polar transport pathways for water and other polar solutes through non-polar polymers. By using nanocellulose in the form of cellulose nanocrystals (CNCs) and a non-polar polymer matrix, composite membranes with a similar polarity gradient to plant cuticles were prepared. These membranes exhibited directional water transport properties and were compared with natural cuticular membranes isolated from olive and ivy leaves.

Having established these asymmetric water transport properties, the impact of this architecture on the permeation of liquid mixtures of ethanol and water was explored for pervaporation applications. CNCs were modified with oleic acid (OLA-CNCs) and also replaced with high aspect-ratio cellulose nanofibers (CNFs) to investigate the effect of surface chemistry and nanofiller morphology on the structural and barrier properties of the nanocomposite membranes featuring nanocellulose fillers.

In summary, the results of this thesis provided new insights on the permeation of water through biological and artificial dense membranes, but also helped us to elucidate the effect of processing conditions, nanocellulose surface chemistry, and filler aspect ratio on the structure-property relationships of nanocellulose composite dense membranes, especially in the context of pervaporation applications.

Jury:

Prof. Dr. Christoph Weder (thesis supervisor)

Prof. Dr. René Rossi (external co-examiner)

Prof. Dr. Michael Mayer (internal co-examiner)

Prof. Dr. Ullrich Steiner (president of the jury)