

## Bio-inspired membranes with well-defined channels

Annarosa Gugliuzza<sup>a,\*</sup>, Valentina Speranza<sup>b</sup>, Francesco Trotta<sup>c</sup>, Erico Drioli<sup>a,d</sup>

<sup>a</sup>Research Institute on Membrane Technology- National Research Council (ITM-CNR),  
Via P. Bucci, Cubo 17/C, I-87030 Rende (CS), Italy. e-mail: a.gugliuzza@itm.cnr.it

<sup>b</sup>Department of Pharmaceutical Science, University of Calabria,  
Via Pietro Bucci, I-87030 Rende, Italy

<sup>c</sup>Department of Chemistry I.F.M, University of Turin  
Via Giuria 7, I-10125 Turin, Italy

<sup>d</sup>Department of Chemical Engineering and Materials, University of Calabria,  
Via Pietro Bucci 45A, I-87030 Rende, Italy

A new bio-inspired and green process based on the principle of the vapor condensation on cold surfaces has been selected for building up next generation membranes. Water droplets have been used like self-assembly building blocks for the creation of well-defined channels through polymeric matrixes. High order and regularity of these 3D patterns resemble those of challenging anodic and lithographed structures. The pore size has been modulated on the microscopic scale length by changing the density of the polymer solution. Membrane topography-surface property relationships have been found. The defined morphological and physicochemical features make these membranes promising interfaces for bio-technological and chemical engineering applications.

### Introduction

Well-defined architectures are in high demand for membrane separations, since the successful outcomes of the processes depend strictly on the intrinsic morphological characteristics of the interface processed (Gugliuzza, 2007). Membranes with well-patterned pores through 3D assemblies have a great potential for sophisticated applications in various fields of the chemistry and bio-chemistry (Gugliuzza, 2008). Water desalination and emulsification are only two examples of advanced technology processes, which use no selective porous membranes to interface two different media at the mouth of the pores, preventing them to mix and promoting diffusive transport through the channels. High control of the membrane structure and surface wetting properties are, therefore, strongly requested for these kinds of process.

A higher structural control meant for the uniformity and regularity of the pore size, shape and sequence represents, for example, an important challenge for the membrane emulsifiers. In this case, the pore structure becomes decisive for the final size and shape of the droplets uniformly dispersed in a continuous medium. On the other hand,

homogeneous distribution of regular multi-channels means also large interfacial area and process uniformity in all regions of the membranes. These factors are significant for the productivity of all membrane contactor process, including one of the most pressing such as the water desalination. In both the cases, controlled mutual membrane-liquid interactions are to be considered in order to preserve the stability of the interface with operational time.

Here, new micro-fabricated self-assembled membranes are proposed and discussed. Three-dimensional porous layers have been prepared by mimicking what daily occurs in nature when humid air matches cold surfaces (Srinivasarao, 2001). Modified poly-(etherether)ketones [PEEK-WCs] (Trotta, 2002) have been patterned in ordered structures by exposing the polymer solutions to humid currents and, then, structure-property relationships have been examined. Membranes with well-patterned and hexagonally packed structures have been generated as the result of an ordered arrangement of imprinting water droplets. Indeed, these templates build up pores with size and shape comparable to those of the spheres. Ordered sequence and uniform distribution accomplish the well-defined morphology of these films, making them promising interfaces for refined applications.

## **Experimental**

### **1.1 Materials and Methods**

Microporous films based on modified poly-(etherether)ketones [PEEK-WCs] have been fabricated by exposing the polymer dopes to moisture (Gugliuzza, 2008). The casting solutions have been cast on clean and dried stainless steel supports and located inside of pre-equilibrated boxes equipped with sensors of temperature and relative humidity (DELTA E Company). The membrane morphology has been investigated by Scanning Electron Microscopy (ESEM, Quanta FENG 200, FEI Company). Pore size and surface porosity have been estimated from SEM images by using Image J 1.37V software. The mean pore size has been calculated from the log-normal plot, while the surface porosity has been calculated from the ratio between the areas of the pores to the total membrane surface area (Gugliuzza, 2008). Membrane topography has been investigated by using the Atomic Force Microscopy (AFM, Nanoscope III Digital Instruments, VEECO Metrology Group). Tapping Mode™ AFM has operated by scanning a tip attached to the end of an oscillating cantilever across 10x10 μm of sample surface at a rate of 1.0 Hz. Kinetic contact angle experiments have been performed by sessile drop method (CAM 200-KSV instrument LTD, Helsinki, Finland). The liquid probe droplets have been dispensed and deposited on the membrane surface by using a micro syringe with automatic dispenser and the images have been captured by a digital camera.

### **1.2 Results and Discussion**

Self-standing membranes have been fabricated according to a bio-inspired green approach like the spontaneous condensation of humid air on cold surfaces (Fig.1). The condensation of water droplets was promoted by a gradient in temperature established at the interface of the casting solution and humid air. After nucleated, the water droplets grew and arranged in ordered lattices and, then, propagated through the liquid film (Fig.2a).

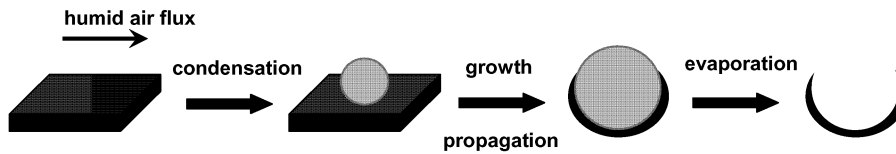


Figure 1 Schematic representation of the imprinting action of water droplets in liquid films.

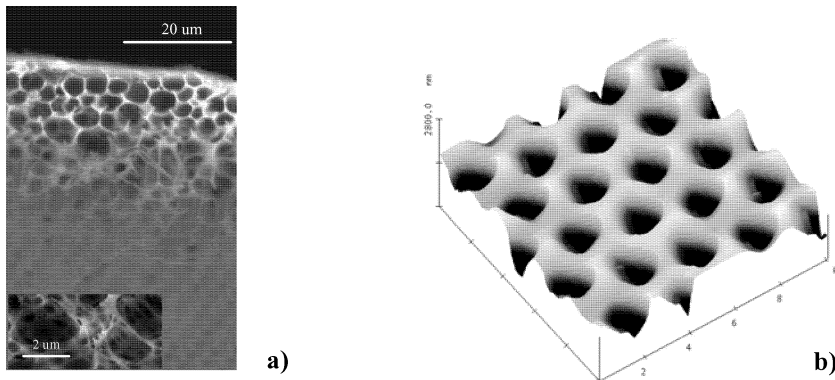


Figure 2 Honey-comb membranes: a) SEM image of the cross-section of the membrane and zoom of the bulk; b) AFM image of the membrane upper surface

The following solvent evaporation led to air-bubble arrays, where interconnected pores resulted enveloped in polymeric networks having a typical honey-comb assembly (Fig.2b).

All membranes exhibit structures with a typical precision of lithographic techniques. Coalescence phenomena have been prevented by the stabilizing action of the polymer at water droplet-liquid film interface. Hence, the pores exhibit highly ordered sequence and reproducible inter-distance, yielding narrow distribution.

The high pore density per membrane area, going up to 80%, provides high interfacial area and promotes high uniformity of the process in all regions of the films, obeying to the contactor technology requirements.

The use of water droplets like spherical building blocks has allowed generating regular and well-shaped pores, whose size has been modulated on the microscopic scale length as a function of the solution density (Fig.3a). At higher density, the permanence time of the droplets on the surface of the liquid film was longer. The slacked propagation through the liquid film promoted, therefore, higher growth of the cross section shape of the top hemisphere of the water droplet in contact with air, resulting in bigger pore size

(Fig.3a). Although the propagation of water droplets through solutions at higher density could be unexpected, 3D self-standing layers have been fabricated (Fig.2a). This behavior might be mainly ascribed to kinetic controlling factors, as suggested by theoretical studies still in progress.

Undoubtedly, the high regularity and order of the channels make these patterns attractive interfaces for membrane contactors. Furthermore, the particular topography of these arrays (Fig.2b) produces additional surface roughness with values around 300 nm, influencing the final membrane surface properties.

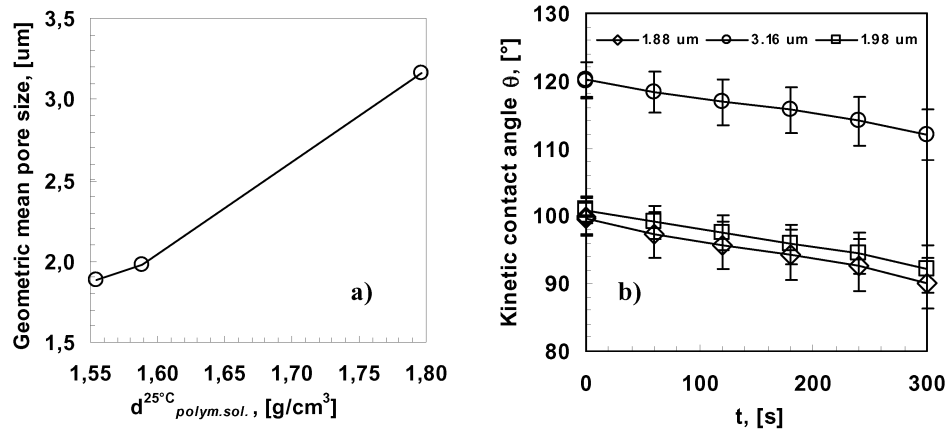


Figure 3 Structure-property relationships: a) solution density as controlling factor for the modulation of the pore size; b) measurements of the liquid water spreading on honeycomb surface with time

This induces the formation of hydrophobic air layers at the membrane-liquid water interface (Gugliuzza, 2007). The result is an increase in the water repellence of the membrane surfaces. Kinetic contact angle experiments have evidenced changes in the wetting properties of the films (Fig.3b), but in all cases the liquid water is prevented from penetrating inside the pores. This provides important indication about the role of the mutual liquid-membrane interactions with time. In this case structure-wetting properties relationships are powerful enough to decide the final performance of these membranes.

## Conclusion

Honeycomb membranes have been fabricated by using a greener, cheaper and shorter in time technique. Anodica alumina-like polymeric patterns have been generated by using imprinting water droplets. Pore size, shape, and arrangement match those of the template, resulting in well-defined multi-channel membranes. The morphological and physicochemical characterizations have provided useful indication about some specific challenging structural features of these films, suggesting their potential use like next generation interfaces in advanced contactor applications.

## References

- Gugliuzza A., Aceto M.C., Macedonio F., Drioli E., 2008, Water droplets as template for next generation self-assembled poly-(etheretherketone) with Cardo membranes, *J. Phys. Chem. B* 112 (34), 10483-10496.
- Gugliuzza A., Drioli E., 2007, PVDF and HYFLON AD membranes: Ideal interfaces for contactor applications, *J. of Membr. Sci.* 300, 51–62.
- Srinivasarao M., Collings D., Philips A., Patel S., 2001, Three-Dimensionally Ordered Array of Air Bubbles in a Polymer Film, *Science* 292, 79-83.
- Trotta F., Gordano A., Drioli E., Musso S., 2002, New derivatives of PEEK-WC for membranes preparation, *Recent research development in applied polymer science*, 529-547.

## Acknowledgement

This work has been carried out within the frame of the research project: European Network of Excellence on Nanoscale-based Membrane Technologies (NoE NANOMEMPRO N.500623-2-26-7-2004).

