

# Sustainable PVDF membranes preparation using $\gamma$ -Valerolactone (GVL) as a green solvent

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**Introduction.** Membrane manufacturing is yet to embrace the use of harmful and toxic solvents, such as N-methyl-2-pyrrolidone (NMP), N, N-dimethylacetamide (DMA), and N, N-dimethylformamide (DMF) despite being a sustainable technology with a low environmental footprint [1-2]. Finding solvents that are more environmentally friendly and sustainable for making polymeric membranes is imperative. In this work,  $\gamma$ -valerolactone (GVL) was selected as a renewable green solvent for the preparation of poly (vinylidene fluoride) (PVDF) membranes by phase inversion technique that allowed to obtain membranes with controlled morphology, pore-size and physical-chemistry properties comparable to those commercially available.

**Experimental/methodology.** PVDF-based membranes were produced by coupling vapor-induced phase separation (VIPS) and non-solvent-induced phase separation (NIPS) techniques. The formation mechanism of the developed membranes was preliminary studied in terms of thermodynamics, related to polymer precipitation behavior (such as Hansen Solubility Parameters), and kinetics, related to the exchange rate of solvent/nonsolvent during phase separation (such as dope viscosity). The PVPK17 (polyvinylpyrrolidone) and polyethylene glycol (PEG200) as pore-formers were used for the fabrication of membranes with controlled pore sizes. The membranes were cast in the climatic chamber with 55Rh% of humidity for different times (0,2.5,5 minutes) Isopropanol and/or Ethanol with water were selected as coagulant baths and the effect of relative energy difference (RED) in different compositions was investigated. The membranes were fully characterized concerning morphology, pore size distribution, wettability, thickness, and porosity.

**Results and discussion.** GVL was used as a green and bio-based solvent for the replacement of the commonly employed for producing PVDF porous membranes with a wide range of pore sizes (from 0.1 to 1  $\mu$ m). The results confirmed an asymmetric structure of the membrane and the possibility of obtaining a sponge-like morphology without the presence of macrovoids depending on dope solution composition and preparation conditions. The top structure changed from dense to porous in the case of the exposure time to humidity was increased from 0 to 2.5 minutes (NIPS-VIPS technique). Generally, the effect of humidity on membrane morphology delays the phase inversion process promoting the formation of porous surfaces and sponge-like structures. The porosity of the membranes was in the range between 84% and 86% with a thickness of about 90-120  $\mu$ m dependent on the composition of the dope solution and, generally, the presence of additives may form thicker membranes. The results of the work are crucial in opening up new opportunities for sustainable membrane fabrication at the industrial level.

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