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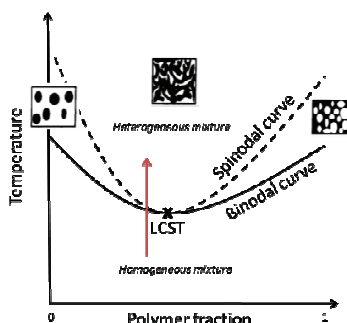
Elaboration of porous PVA membrane by TIPS-LCST process without using organic solvent

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Introduction

Porous polymeric membranes are classically made by phase inversion processes: non-solvent induced phase separation process (NIPS), dry casting process or UCST-TIPS process (reduction of temperature under the critical solution temperature) [1]. Nowadays, all these elaboration processes involve a large quantity of organic and often toxic solvents needed for the initial dissolution of the polymer. This implies to proceed cautiously to avoid pollution (spoiling, accidental contamination or evaporation losses) and to restrict environmental and public health impacts.

The aim of this study was therefore to elaborate new membranes without organic solvent. The challenge was to prepare porous membranes by using a hydro soluble polymer leading free materials. We developed an original preparation process based on phase inversion induced by an increase of the temperature Lower Critical Solution Temperature, TIPS process (figure 1). After phase separation the polymer was cross-linked in order to solubility into water and to set the network for further applications.



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Figure 1: phase diagram of TIPS-LCST process

Two different polymers were selected in our laboratory to develop this green process: (i) the hydroxypropyl cellulose (HPC), a bio sourced polymer with a complex structure and low structuration dynamic (ii) the polyvinyl alcohol (PVA), a synthetic polymer used in this work.

PVA was selected because (i) it is soluble in water when hydrolyze degree (HD) ranges from 70 to 90 % (ii) it is characterized by a moderate LCST in water solution [2], (iii) it is well known for its good film-forming properties and (iv) it is a non toxic, biocompatible and biodegradable polymer. In order to reduce the energy costs induced by the temperature rising during the phase inversion process by LCST-TIPS, PVA could be combined with saline solution to promote a salting out effect and lower the LCST. The crosslinking of the polymer chains was achieved by addition of glutaraldehyde (GA) in the polymer solution to create bonds between the molecules in the polymer chain by reacting with -OH groups [3].

Material and methods

In this study, PVAs with two different hydrolyze degrees were used: PVA72 (with 72% HD) supplied by Synthomer and PVA88 (with 88% HD) supplied by Sigma Aldrich.

PVA solutions were prepared by dissolving PVA in water at 70°C under stirring during 3 hours; the polymer solution was then cooled at ambient temperature. The determination of the lower

critical solution temperature was performed using transmittance measurements versus temperature by an UV spectrometer at 600nm.

For membrane elaboration, GA (0.5 % wt.) and HCl (0.3 % wt.) were added into the PVA solution to ensure the cross-linking. The solution was immediately cast onto a glass plate placed on a heating support between 60 and 80°C, and the initial thickness was controlled (between 200 and 1500 μm) using appropriate casting knives. After phase separation, water was removed by evaporation and the membranes were washed with de-ionized water for removing HCl and unreacted GA.

Membranes were characterized by (i) Scanning Electron Microscopy (SEM) Hitachi S-4800 for cross-section photographs, (ii) mechanical properties using an Anton Paar rheometer and (iii) filtration tests using Amicon cells.

Results

LCST of PVA-water solution

Figure 2 (a) presents the binodal curve of water-PVA72 solutions for increasing polymer concentrations from 0 to 35 wt%. According to this phase diagram, the temperature was set between 60 and 80°C to ensure phase separation for membrane preparation despite solvent evaporation. The demixing of the polymer solution was achieved by spinodal decomposition inducing the formation of bicontinuous structures.

Figure 2 (b) represents the effect of NaCl addition on phase separation temperature, in PVA88 solution which does not present LCST under 100°C without salts. Addition of salt reduces strongly the LCST of PVA solution up to the ambient temperature. In fact, NaCl acts on the quality of solvent by modifying hydrogen bonds between water-polymer and polymer-polymer.

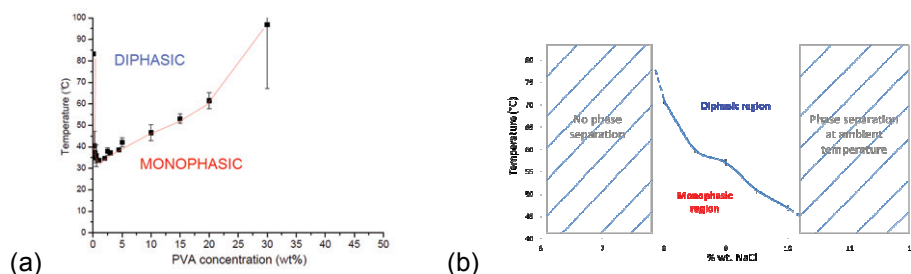


Figure 2: (a) phase diagram for PVA72 – (b) phase diagram for PVA88 with NaCl

Membrane elaboration and structure control

Preliminary tests allowed us to select a concentration of 10 wt% for PVA72: the polymer solutions were characterized by a low LCST (45°C) and offered acceptable casting ability. As presented in table 1, it was possible to adjust membrane morphology by controlling the elaboration temperature: dense structure and impermeable membrane (for pressure up to 3 bars) were obtained at ambient temperature (< LCST) whereas porous structure and permeable membrane were elaborated at temperatures higher than the LCST. Such porous membranes were characterized by a permeability that depended on the operating conditions such as temperature, the time under heating and the salt concentration. The membranes displayed good mechanical properties, i.e. the tensile stress at break was measured between 1 and 4 bars. These values were suitable for micro- and ultrafiltration [4].

PVA 10 wt% – GA 0.5 wt% – HCl 0.1 M	
Ambient temperature	60°C – 70°C – 80°C

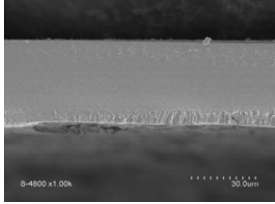
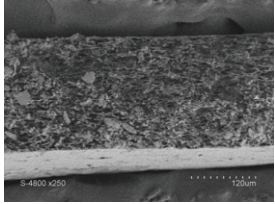
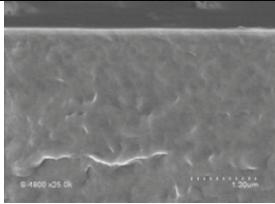
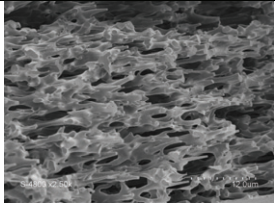
Cross-section microstructure		
Structure (zoom)		
Water permeability	Not permeable	–up to 10000 L.h ⁻¹ .m ⁻² .bar ⁻¹ by controlling others process parameters

Table 1: Impact of operating parameters on membrane properties

In this work, we successfully developed porous PVA membranes without using organic solvent and we showed that these membranes could be used for micro- and ultrafiltration. Improvement of the functional properties of these membranes is currently in progress.

[1] P. Van de Witte et al, *Journal of Membrane Science* 117 (1996), 1-31

[2] B. Briscoe et al, *Polymer* 41 (2000), 3851-3860

[3] B. Bolto et al, *Progress in Polymer Science* (2009), 969-981

[4] L.J. Zeman et al, *Microfiltration and Ultrafiltration : Principles and Applications* (1996)

Keywords: Polyvinyl alcohol, Free solvent process, TIPS-LCST process, Porous organic membrane