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**Formation of polymeric porous membrane without organic solvent by thermally induced phase separation in LCST system (hydroxypropylcellulose/water)**

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**Introduction.**

Phase separation using (i) non-solvent coagulation of a polymer solution (NIPS or VIPS process) or (ii) temperature decrease (TIPS process) is the most widespread industrial process to manufacture membranes. Large solvent quantity is usually used whatever the process, hence leading to environmental and health problems. Since the polymer concentration is usually in the range 15-20% and since coagulation and washing baths require being often renewed, large amounts of aqueous solutions must be treated.

So, this work aims at developing a novel process for producing free organic solvent membranes, in agreement with the principles of green chemistry.

**Methods.**

In this respect, hydroxypropylcellulose (HPC) was used since this polymer is (i) bio-sourced and (ii) soluble in water at ambient temperature. Moreover, HPC is characterized by a moderate Lower Critical Solution Temperature (LCST) (Figure 1). Consequently, in this work, porous membranes from HPC/water system were made by an original technique: the LCST-TIPS process, where the phase separation by spinodal decomposition was induced by heating the polymer solution over the LCST. Consolidation of the film structure was carried out by chemical cross-linking using glutaraldehyde (GA). HPC membranes were studied for different operating conditions (formulation and process parameters) and they were characterized at different levels: morphological properties by Scanning Electron Microscopy (SEM), dynamic mechanical properties, thermo-gravimetric analysis and filtration tests using Amicon stirred cells.

**Results and discussion.**

The phase diagram for HPC/water system was assessed by UV/visible spectrophotometry (with a programmed temperature controller); cloud point temperatures were measured by following the transmittance of HPC solutions at 600 nm.

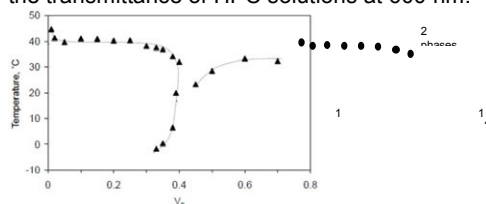


Figure 1: HPC/water phase diagram - ▲ [1]; ● UV visible measurements

The experimental data were compared with results given by Marsano and co-workers [1] (Figure 1). Despite the complexity of phase diagram of HPC/water system, a good agreement was observed between the experimental measurements and the data from literature in the range of polymer volume fraction [0-0.35], i.e. before liquid crystalline phase behaviour.

Figure 1 points out non classical phase diagram since the binodal temperature is almost constant in a large range of polymer volume fraction, whereas the LCST classically increases with increasing the polymer concentration. Such behaviour is interesting for membrane elaboration since the energy cost for inducing the phase inversion at high polymer concentration keeps moderate.

HPC membranes obtained at 60 °C with a weight composition of 20% HPC, 5% GA and 1% HCl used as catalyser, show a bicontinuous structure constituted by a porous surface over cavities with some tortuosities (Figure 2). Thermal stability of HPC films pointed out two degradation stages, the first one (at 60 °C) corresponding to the water loss of films and the second one (at 329 °C) being due to the cellulose ethers degradation of HPC, the decomposition (thermal and oxidative) and elimination of volatile GA compounds.

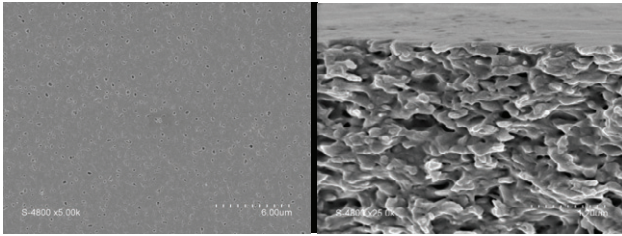


Figure 2: Surface (a) and cross-section (b) SEM views of HPC films formed at 60 °C

Mechanical properties of HPC films are summarized in table 1. Comparing to uncross-linked HPC films, the Young module values exhibit that the addition of 5% GA did not enhance the rigidity of cross-linked HPC films that remain flexible, GA is not overdosed. Moreover, the tensile strength and elongation at break are higher for cross-linked HPC films. By connecting macromolecular chains, the cross-linker improves mechanical properties of HPC films.

Table 1: Mechanical properties of HPC cross-linked and uncross-linked films at 25 °C and air dry conditions

Conditions	Tensile strength	Maximum elongation	Young Module	Thickness
HPC20% / GA 5%	5.30 MPa	8.69%	610.50 MPa	50 $\mu\text{m}$
HPC 20% / GA 0%	1.86 MPa	0.68%	620.60 MPa	48 $\mu\text{m}$

To perform permeability tests under pressure, polymer solution was cast onto a non woven support, as classically done for industrial organic porous membranes. The sub layer of the membrane acts as a mechanical support and offers maximum elongation values reaching 35%. Water permeability tests highlight a resistance to pressure up to 4 bars with a good linearity in the evolution of water flux as function of applied pressure. Permeability values obtained in such conditions ( $20 \pm 2 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ ), lower than typical ultra-filtration values, are linked to the presence of a thin dense layer at the top surface. Hence the main perspectives of this work concern the enhancement of the permeability by controlling membrane morphology thanks to operating conditions (formulation and process).

This work represents the first study to investigate TIPS-LCST process for the formation of porous polymer membranes with no organic solvent for water filtration applications.

[1] Phase diagram of water soluble semirigid polymers as a function of chain hydrophobicity. E. Marsano, G. Fossati. *Polymer* 41 (2000) 4357-4360.

Keywords: Hydroxypropylcellulose, Porous membrane, TIPS (Thermally Induced Phase Separation), LCST (Lower Critical Solution Temperature)