

## POLYMERIC MEMBRANES FOR TREATMENT OF PRODUCED WATER ON OFFSHORE PLATFORM

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### Introduction

Phase separation using non-solvent coagulation of a polymer solution is the most widespread industrial process to manufacture membranes. Large solvent quantity is then used that complicates the overall process and may lead to environmental and health problems. Knowing that polymer concentration is usually in the range 15-20 % and coagulation and washing baths require to be often renewed, large amounts of aqueous solutions must be treated. For instance 10 m<sup>2</sup> of ultrafiltration membrane need about 1 to 1.5 kg of solvent.

Our objective in this proposal is to develop a novel process for membrane mass production in agreement with the principles of green chemistry. The main technical and economic output of using water instead of organic solvents should consist in a simplification of the manufacturing process by lowering wastes and recycling. Environmental outputs will be a safer process, more economic on atoms, limiting the wastes and applicable to renewable naturally-occurring polymers.

The aim is to prepare membranes using either water-soluble commercial polymer like cellulose ethers presenting a lower critical solution temperature (LCST). Consolidation of the film structure will be carried out by chemical crosslinking. Mastering this process is very appealing but needs the following requirements: (i) to fully understand how phase separation proceeds for various polymers in water as temperature is raised above their LCST; (ii) to establish the relationship between phase separation mechanism, processing parameters during membrane preparation and morphology of final membrane; (iii) to determine the permeation performances of the obtained membranes.

### Membrane formation

The most widely used method to prepare polymeric membranes is intrusion of a non-solvent into the polymer solution. This process is called Non-solvent Induced Phase Separation (NIPS). The non-solvent, usually water, can be introduced to the polymer solution either in the vapour form (Vapour-Induced Phase Separation, VIPS) or in the liquid form (Liquid-Induced Phase Separation, LIPS).

However, the separation can be also achieved by changing the temperature of the solution. This process called Thermally Induced Phase Separation (TIPS) is realized by fast-decreasing the solution temperature to reach the phase demixing domain located in the lower part of the phase diagram.

Actually, binary polymer-solvent phase diagram can exhibit phase separation both at low and high temperature. In the first case, the polymer solution is characterized by an Upper Critical Solution Temperature (UCST) and phase separates by decreasing the temperature.

On the opposite, several systems such as HydroxyPropyl Cellulose/water system (the system chosen in this work), present a Lower Critical Solution Temperature (LCST) and phase separation takes place by increasing the temperature (cf. Figure 1).

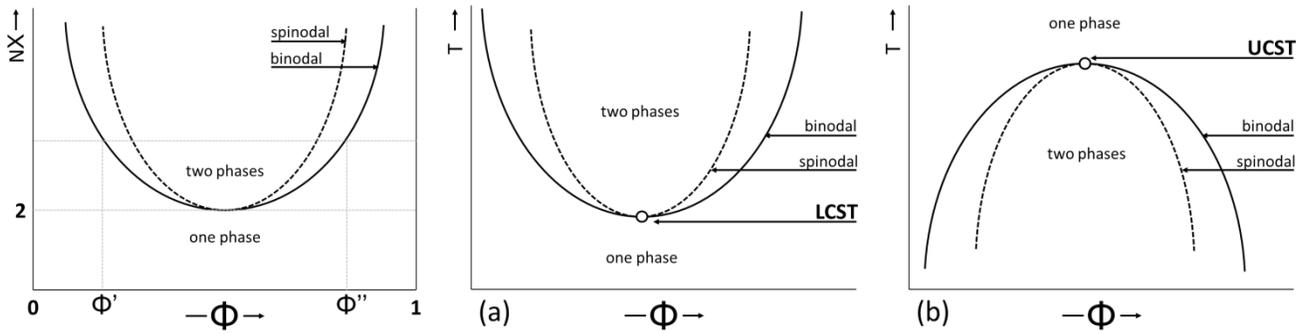


Figure 1 : Phase Diagram of thermosensible polymer, (a) LCST, (b) UCST [1]

Figure 1 show phase diagram of thermosensible polymer with the Flory interaction parameter:

$$\chi(T) \cong A + \frac{B}{T}$$

The phase diagram of the HPC/water system is represented in Figure 2.

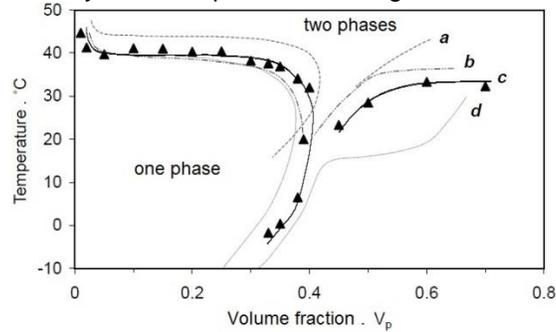


Figure 2: Phase Diagram of HPC in water: (a) from [2]; (b) from [3]; (c) from [4]; (d) from [5]

The critical temperature before phase separation is around 40°C until 0.4 volume fraction, between 0.5 and 0.7 the phase separation temperature is higher than 35°C.

### Membrane formation

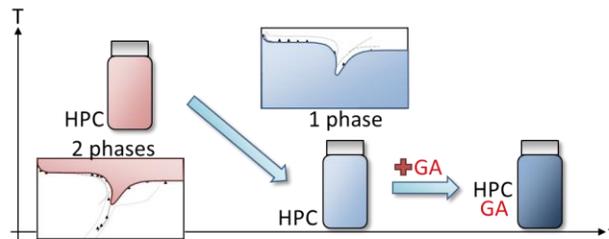


Figure 3: Polymer (HPC) solution preparation

In the first step, HPC powder is pre-slurrying in a nonsolvent (hot water – 60°C), the solution is stirred until complete homogenization. Then, the solution was mixed at room temperature for optimizing the dissolution of the whole particles. Then, the Glutaraldehyde was added under agitation (Figure 3).

After 24 hours (bubbles removal), Chlorhydric acid (HCl) was added as a catalyst for crosslinking. The solution was cast onto a glass plate for the membrane elaboration.

### Mixing evaporation/crosslinking/evaporation

The cast thin polymer film is placed on a heated plate at 60°C. When the HPC reached its critical temperature, the phase separation started and formed the porous structure.

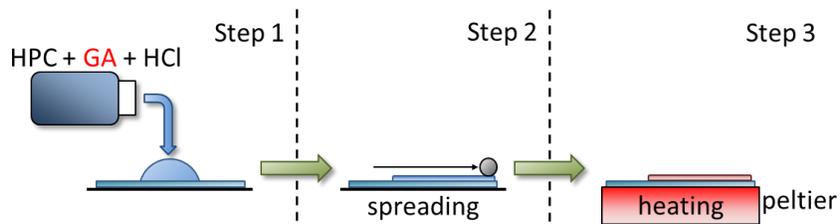


Figure 4 : HPC membrane elaboration process

Three phenomena occur during the heating step (3):

- Phase separation: Lowering the temperature induces phase separation by spinodal decomposition which constitutes the membrane structure.

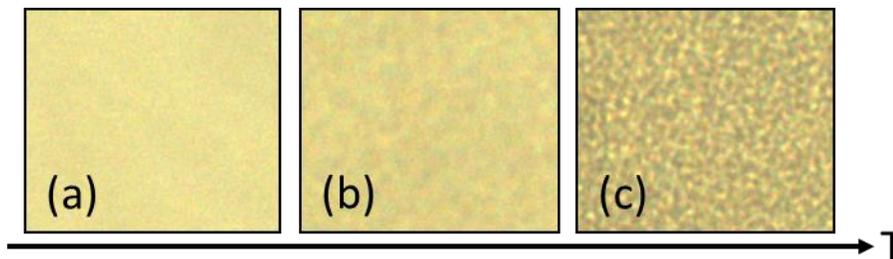


Figure 5 : Observation of spinodal decomposition by optical microscopy

Figure 5 shows the structure change before and after the phase separation. Figure 5.a represents a monophasic system, the temperature was lower than the LCST, the structure changes with increasing temperature. In Figure 5.b, the temperature was close to the LCST, therefore the phase separation started. In Figure 5.c, after exceeding the LCST, a stable inhomogeneous structure is noticed. Those pictures can be analyzed in the purpose to determinate the structure growth laws, which was not detailed herein.

- Evaporation: During the phase separation, an over phenomenon is present: the solvent evaporation that occurred concomitantly with phase separation. Evaporation phenomena induced an increase of the polymer volume fraction during the process, and promoted the crosslinking reaction. Nevertheless, the evaporation was not expected to affect the phase separation temperature. Indeed whatever the composition path (in relation with fast or slow evaporation), the cloud point temperature is almost constant, between 25 and 40 °C (Figure 6).

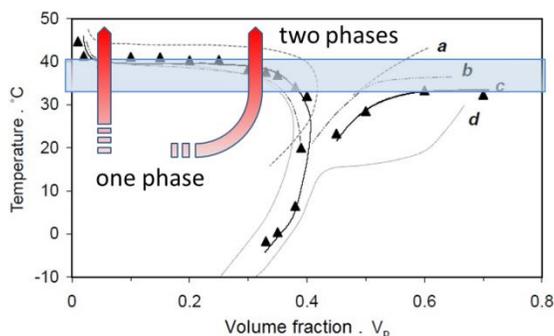


Figure 6 : potential composition paths during LCST phase separation

- Crosslinking: As aforementioned, polymeric membranes made from HPC/water system were prepared using LCST-TIPS method and a chemical crosslinking was performed using Glutaraldehyde (GA). The chemical crosslinking aimed at (i) preventing the membrane dissolution in water solution in filtration operation and (ii) fixing the membrane morphology to obtain a porous structure. The mechanism of chemical crosslinking between GA and HPC is explained in Figure 7.

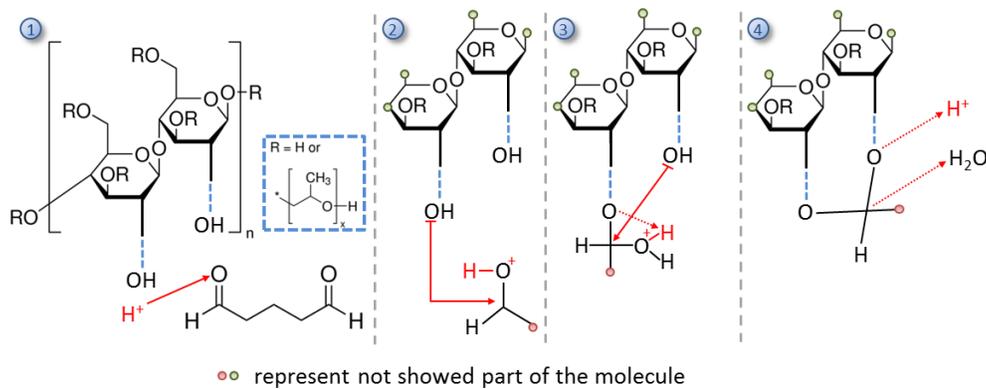


Figure 7: Chemical crosslinking between Glutaraldehyde and HydroxyPropyl Cellulose.

HPC is stable, so it needs a catalyst (HCl) to initiate the crosslinking reaction.  $H^+$  ion liberate by the HCl attacks the oxygen and make it bound with carbon weaker. Then, the OH on HPC can attack GA carbon. This reaction releases a molecule of water ( $H_2O$ ) and let the other HPC OH to link the GA carbon. At the end, an  $H^+$  ion is released in the water for another reaction.

A competition between these three phenomena constitutes a scientific lock. The heating is the most important parameter during the membrane process, since it affects both evaporation and crosslinking. (cf. Figure 8)

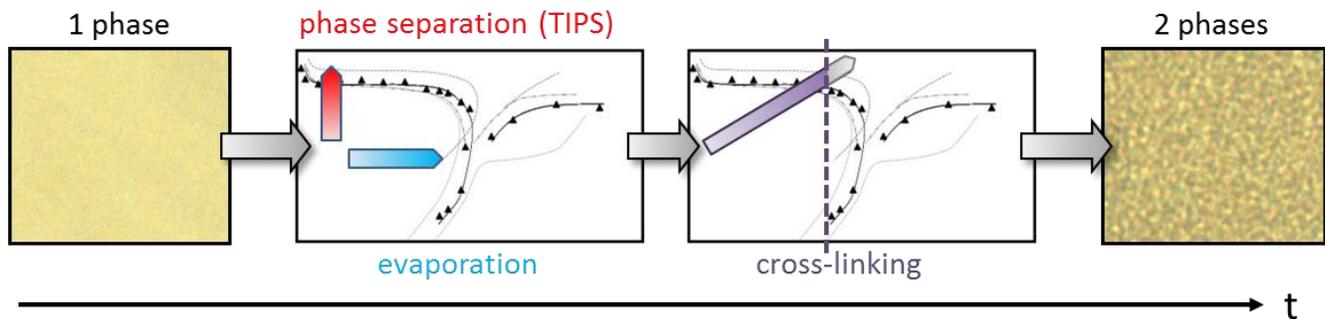


Figure 8 : Phenomena involved in the TIPS-LCST process.

- If the heating rate is too high, the membrane will dry before the end of phase separation and the crosslinking will occur too early (unfinished structure).
- If the heating rate is too low, the crosslinking will begin whereas phase separation was not totally complete.

Furthermore, this work exhibited that the solvent evaporation favored the chemical crosslinking, by making the polymer chains closer.

#### Membrane structure

After the membrane formation stage, HPC membranes were characterized by SEM (Figure 9).

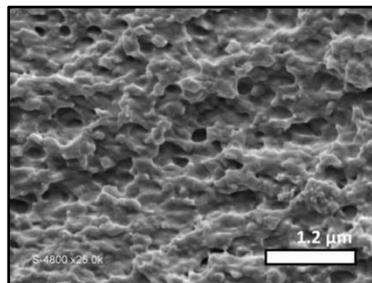


Figure 9 : SEM picture of HPC membrane (section).

A porous structure can be observed, it was obtained by phase separation due to spinodal decomposition. The phase separation shown in Figure 5 leaves a bi-phasic structure, after the evaporation of the aqueous phase, a porous structure was obtained. It confirms that the crosslinking step begin after the phase separation. With this information, the study can be focused on the characterization of this free organic solvent membrane.

### Swelling

The stability of HPC membranes must be defined before use for water filtration, swelling measurements can give an accurate result. A list of solvent has been used to determine the swelling and re-solubilization ratios [6].

cf. *Tableau 1* Tableau 1

*Tableau 1: Swelling and re-solubilization ratio into different solvent (7 days).*

Solvent	Water	Acetic Acid	Acetone/water	Chloroform	Ethanol	Methanol
Swelling ratio (%)	6	26	31	18	12	10
Re-solubilization (%)	0	20	4	9	8	12

The swelling ratio of HPC membrane into water after 7 days shows that the crosslinking was efficient. Into water, it did not have any re-solubilization. It confirms the possibility to use an HPC membrane for water filtration.

### Filtration

The HPC membrane is tested with a dead-end filtration system (Figure 10). The pressure is controlled by a manometer (1) which pushes the tank solvent (2) into the filtration cell (3), the filtrate solvent (4) is weighed (5). With the weigh variation over time, the membrane flux can be determinate.

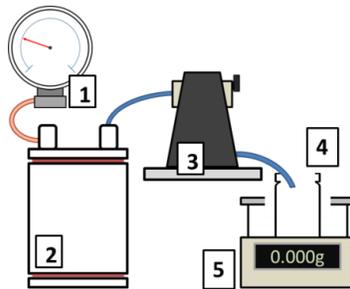


Figure 10 : Dead-end filtration system

First at all, a conditioning is requisite to open the membrane porosity, and then the filtration measure can begin.

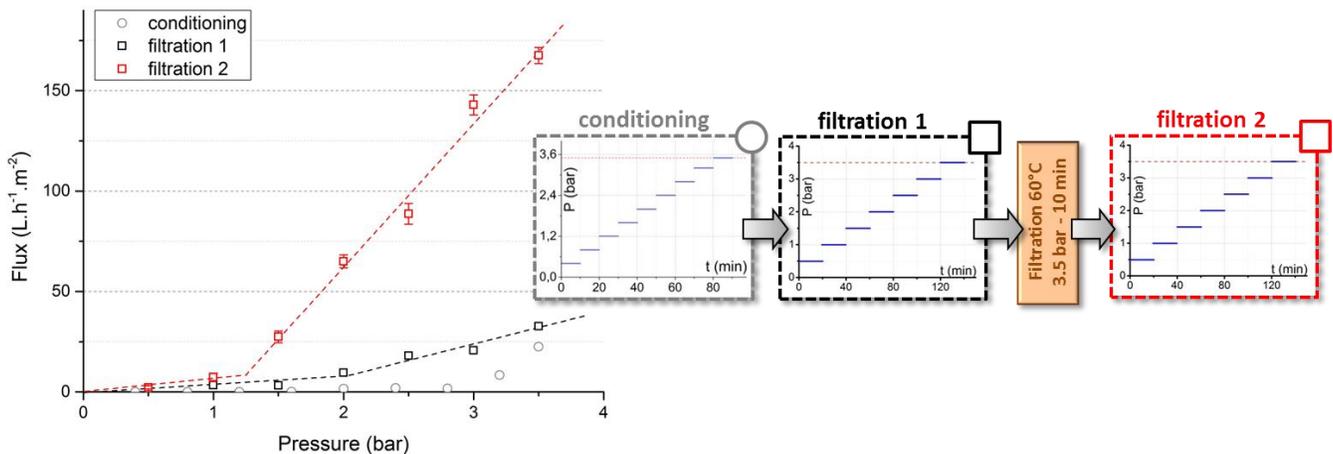


Figure 11 : HPC membrane behavior (flux  $[L \cdot h^{-1} \cdot m^{-2}]$  versus pressure [bar])

A first filtration stage was done at room temperature, the obtain flux was between 0 and 40  $L \cdot h^{-1} \cdot m^{-2}$  (cf. Figure 11) for a maximum pressure of 3.5 bar, in the lower limit of ultrafiltration [7]. Thermal treatment was then

performed to enhance the membrane flux (10 minute at 3.5 bar – 60°C) - beyond 40°C water become a non-solvent, the porosity opening was expected to be far easier than a filtration at room temperature. A second filtration was done after the thermal treatment, Figure 11 shows that the membrane flux was improved to 160 L.h<sup>-1</sup>.m<sup>-2</sup>. This result not only proved that a thermal treatment could enhance the membrane flux, but also demonstrated that this polymeric membrane was able to support a temperature at 60°C.

#### Conclusion

This work demonstrated that a porous and stable membrane could be formed from water-soluble polymer, i.e. without organic solvent in the formulation. The HydroxyPropyl Cellulose – a biosourced polymer – was used within a green processing membrane formation. The whole process was thought in the aim to never consume organic solvent, the LCST properties of HPC is an original way to reach this objective.

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