



Fabrication of novel porous membrane from biobased water-soluble polymer (hydroxypropylcellulose)



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ARTICLE INFO

Keywords:

Membranes
Green chemistry
Biobased polymer
Water-soluble polymer

ABSTRACT

Herein, a novel polymeric porous membrane was developed, without the use of any organic solvent in the initial dope solution and using a biobased polymer derived from cellulose: Hydroxypropylcellulose (HPC). HPC was dissolved in water (20 wt%) and the phase separation was induced by increasing the temperature above the Lower Critical Solution Temperature (LCST) of the polymer solution, around 40 °C in the concentration range concerned in this study. To fix the membrane morphology and to prevent any resolubilization in water during filtration tests, a chemical crosslinking was performed using Glutaraldehyde. The phase diagram of HPC/water system was first studied and not only the cloud point but also the spinodal curves were determined using optical transmission techniques. It was exhibited that HPC phase diagram is very weakly dependent on concentration up to large concentrations and that the metastable region is very small, i.e. the cloud point and the spinodal curves are very close in a large range of concentration. The membrane stability was tested in water and some organic solvents, thus demonstrating the efficiency of the chemical crosslinking during membrane formation. The swelling and mechanical properties of HPC membranes were also investigated depending on the operating condition during membrane formation, showing that the temperature ramp during the membrane formation, from initial to final temperature, have a significant effect on the crosslinking efficiency and hence on the swelling properties. Finally, adding a porogen (PEG200) into the colloid, filtration tests were performed and exhibited that the membrane filtration properties depend on the temperature ramp as well, showing higher water flux for the highest temperature ramp tested.

1. Introduction

Membrane separation technologies are nowadays extensively used in many engineering applications including water treatment and purification. Polymeric membrane materials account for a large majority (ca 85%) of the membrane material demand. Within the polymeric membrane segment, synthetic polymers including polysulfone, polyimide, nylon, polyacrylonitrile, PVDF and others dominate the market. Polymer phase separation, which consists of lowering the solvency of the solvent to the polymer, is mostly used in manufacturing of such porous materials: a dope solution, i.e. a polymer dissolved in a solvent, is cast as a film on a support or extruded as a hollow fiber. Subsequently, a change in the thermodynamic state disturbs the solution equilibrium. Thermally Induced Phase Separation (TIPS) and Non-solvent Induced Phase Separation (NIPS) are the most convenient and common methods for manufacturing porous polymeric

membranes. Many membrane structures can be formed depending on operating conditions (process parameters) and system properties (formulation) [1–3]. NIPS process (including immersion precipitation and Vapour Induced Phase Separation, VIPS) consists of adding a non-solvent into a binary polymer/solvent solution. TIPS process is classically conducted by cooling a hot polymer/solvent solution, inducing thermodynamic instability and thereby phase separation [4–11]. Porous membranes are thus produced by phase separation from polymer solutions and from economic point of view, water is generally used as the non-solvent. 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. For instance, 10 m² of ultrafiltration membrane need about 1–1.5 kg of solvent. The major fraction can theoretically be recycled after an expensive distillation stage (ca 90% for slightly volatile solvents), a fraction is lost by evaporation in air (not negligible for

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highly volatile solvents and high temperature process) and the last fraction is sent for wastewater treatment. Moreover, the use of organic solvent in the membrane formation has consequences on industrial fabrication units, which must be adapted to protect workers from solvent toxicity. Therefore, the use of organic solvents has a significant cost input in the process of membrane manufacturing apart the environmental and public health impact. Facing the challenges of decreasing these impacts, shift of paradigm is needed from conventional solvents towards greener ones including bio-based solvents, ionic liquids and supercritical carbon dioxide [12,13]. Among them, water is obviously the safer and the less demanding on energy. Nevertheless, to the best of our knowledge, very few papers have been devoted to the membrane preparation in water [14–16].

In this respect, the present work aims at preparing polymeric membranes using water as the solvent. This objective clearly addresses the issue of designing greener processes avoiding the use of organic solvents, one of the cornerstones of the green chemistry area. The other objective is to design membrane from bio-sourced materials. The economy of atoms and reduction of energy in the manufacturing of membranes is assumed to be achieved in a friendly environmentally approach using (semi)natural and water-soluble polymers. Cellulose ethers fulfill these criteria. These derivatives are characterized by a lower critical solution temperature (LCST) that can be used to induce the phase separation. The polymer phase separates through a temperature increase above the LCST [17], calling the process LCST-TIPS in contrast to the commonly used upper critical solution temperature (UCST)-TIPS for membrane preparation with synthetic polymers. Phase separation with LCST systems can usually be tuned at moderate, close to ambient temperatures, limiting energy consumption. The available literature on the LCST-TIPS process is very limited. Qin and coworkers prepared membrane from polyethersulfone/poly(vinyl pyrrolidone) K90/N, N-dimethylacetamide (DMA)/1,2-propanediol (1,2-PD) system [18,19] and cellulose acetate/poly(vinyl pyrrolidone) 360 K/N-methyl-2-pyrrolidone (NMP)/1,2-propanediol system [20]. Recently, free organic solvent membranes have been prepared from PVA/water system [16].

Hydroxypropylcellulose (HPC), non-ionic ether of native cellulose, is a polymer with temperature dependent water solubility. Thanks to its renewable origin, ease of production, non-toxicity and optical properties, HPC is widely used (i) for the preparation of dosage forms and coatings, (ii) as viscosity modifier in many product formulations [21]. Furthermore HPC is studied in polymer physics for its lyotropic liquid crystalline phase behavior [21]. HPC has also been largely studied to develop hydrogels for controlled release of active substances above its LCST [22–24].

In this study, porous membranes prepared by LCST-TIPS process from HPC will be demonstrated. The dynamics of membrane formation, including the coupling between the phase inversion dynamics, the crosslinking and the mass transfer by evaporation will be discussed. Since this polymer was poorly studied in the past, the phase diagram was investigated, including both the determination of the cloud point curve and the spinodal curve using light scattering techniques. The membrane morphology of HPC membranes was reported and discussed as a function of the operating parameters including the initial formulation and the temperature ramp. The stability and the mechanical properties of the membranes were then investigated. Finally, preliminary filtration tests in water will be presented.

2. Experimental

2.1. Materials

Hydroxypropylcellulose (HPC) was obtained from Sigma Aldrich (Fig. 1). Its average molecular weight, determined by size-exclusion chromatography, was M_w 80,000 g/mol. Distilled water was used as solvent in polymer/solvent system. The washing bath was exclusively

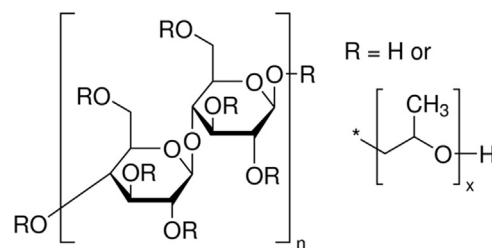


Fig. 1. Chemical structure of HPC ($R = -H/-CH_2CH(OR)CH_3$ with $R' = -H/-CH_2CH(OR)CH_3$).

composed of distilled water. Glutaraldehyde (GA solution 25 wt%) was chosen as the crosslinking agent, hydrochloric acid (HCl solution 37 wt %) as the crosslinking reaction catalyst and polyethylene glycol M_w 200 g/mol as porogen (PEG200). All of these products were purchased from Sigma Aldrich and all the reagents were used without further purification.

2.2. Methods

2.2.1. Preparation of polymer solutions

Hydroxypropylcellulose (HPC) aqueous solution was prepared by dispersing HPC powder in distilled water preheated at 60 °C under magnetic stirring. The initial HPC concentration in water was 20 wt%. The dispersion was then cooled to ambient temperature to promoting polymer dissolution and obtaining homogeneous polymer solution. A given amount of additives was then blended into the solution under magnetic stirring. The solution prepared was degassed under static conditions at 4 °C overnight. The polymer concentration (20 wt%) was chosen in order to reach a convenient viscosity for casting the solution onto the glass plate (the viscosity of HPC solutions was equal to 18.98 Pa s during casting) and to have a moderate cloud point temperature (close to 40 °C). The chemical crosslinker, Glutaraldehyde, was added in the collodion, at a concentration of 0.5 wt% (versus the total solution weight). The catalyzer, HCl, was added just before casting the polymer solution onto the heating plate. HCl concentration in the collodion was equal to 1 wt%. The composition of the polymer solution (see Table 1) was fixed from previous study of Suto *et al.* [35] to optimize the crosslinking, i.e. to obtain an isotropic membrane with well distributed chemical bonds in the whole membrane: Glutaraldehyde weight ratio $1/4$ (GA/HPC) was shown to be the most efficient ratio for obtaining a stable polymer matrix. The concentration of each component in the collodion was summarized in Table 1.

2.2.2. Cloud point measurements

Polymer solutions were prepared by weighing at different concentrations and put after thorough mixing and heating/cooling steps in quartz cuvettes. These cuvettes were immersed in a water thermostated bath at a temperature in the one-phase region. The temperature was then progressively increased by steps of 0.5 °C per 30 min. A laser beam is sent through the cuvette and the transmission of the beam is measured as a function of temperature by means of two photodiodes, one as a reference of the incident beam and the second on the transmitted path.

2.2.3. Membranes preparation

The blend solution was cast onto a glass plate at room temperature

Table 1
Concentration of polymer and additives in the collodion.

HPC	GA	HCl	PEG200
20 wt%	0.5 wt%	1 wt%	5 wt%

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