

SUPERCRITICAL CO₂ DRYING OF POLYSACCHARIDIC MEMBRANES PRODUCED IN IONIC LIQUID: APPLICATION TO CELLULOSE AND CHITIN

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Abstract. New generation processes of solid chitin and cellulose using ionic liquids have been studied. Butyl Methyl Imidazolium Acetate ([BMIm]Ac) has been chosen to be the solvent of both polysaccharides. The main steps of the process are the following:
-step 1: gelation of ionic liquid and solute solution at room temperature,
-step 2: extraction of the solvent and membrane formation by addition of an anti-solvent (water or ethanol),
-step 3: drying of the membrane with supercritical CO₂ (extraction of the anti-solvent and ionic liquid residues).
The solids before and after processing have been characterised by different techniques: Fourier Transform Infra-Red Spectrophotometry (FTIR), and Scanning Electron Microscopy (SEM). Preliminary measurements of the solubility have been done as function of temperature: at 70°C, the saturation is 9 g/100g solution for chitin and 16.5 g/100 g solution for cellulose. A method based on the conductivity measurement has been set up to follow the extraction of ionic liquid during step 2 and to quantify the ionic liquid residue in the membrane. A complete ionic liquid removing is necessary since, residues induce alteration of the solid. The drying by supercritical CO₂ permits to remove the major part of the anti-solvent and ionic liquid in the membrane. A porous and compact membrane is obtained.

Key-words. ionic liquid, chitin, cellulose, gel, supercritical drying, membrane

1 INTRODUCTION

Cellulose and chitin are the most abundant biopolymers in the world and are useful in a lot of applications such as: medicine, food industry, agriculture, waste and water treatment [1, 2, 3]. They are not toxic, biodegradable and constitute renewable resources. However, they are not soluble in the conventional organic solvents such as water or alcohol. They are soluble in mixtures such as Dimethyl Acetamide/Lithium Chloride (DMAc/LiCl) [4, 5, 6] and the transformation processes of these polymers are polluting [7]. For these two reasons their potential applications are limited.

In this context, ionic liquids received much attention because a broad variety of polysaccharides (cellulose [8, 9], chitine/chitosane [10, 11], cyclodextrins [12], starch and zein protein [13], keratin [14], dextrin, amylose and inulin [15] ...) have a large solubility in ionic liquids (between 1 and 20% w/w). Several studies investigated the dissolution of these polymers – this is the case for cellulose in chloride based ionic liquids [16, 17, 18].

Ionic liquid is an organic melted salt – generally liquid at room temperature. It has a negligible vapour pressure and a good thermal stability. It could be used in different applications including crystallisation, gas and liquid separation, chemical reactions [19, 20] instead of classical volatile organic solvent. One particularity concerns the large amount of CO₂ that could be dissolved in ionic liquids under supercritical conditions without volumetric expansion [21, 22, 23].

These properties make them good candidates to develop new green or almost green processes. In this study, we have chosen cellulose and chitin as the solutes, Butyl Methyl Imidazolium Acetate ([BMIm]Ac) as the solvent (Fig-1 (a), (b), (c)) and water as the anti-solvent.

Regeneration process of solid chitin or cellulose dissolved in [BMIm]Ac was studied. This process could be divided in three steps: (i) the solid is dissolved in ionic liquid at controlled temperature, (ii) a gel is formed by cooling at room temperature in humid air, (iii) a membrane or a film is obtained by washing the gel in water or ethanol and (iv) extraction of residues of water/ethanol and ionic liquid with supercritical CO₂.

The combination of water with a hydrophilic ionic liquid offers many advantages: easy recovery of the ionic liquid after the process, the total miscibility and the “green” characteristic of water.

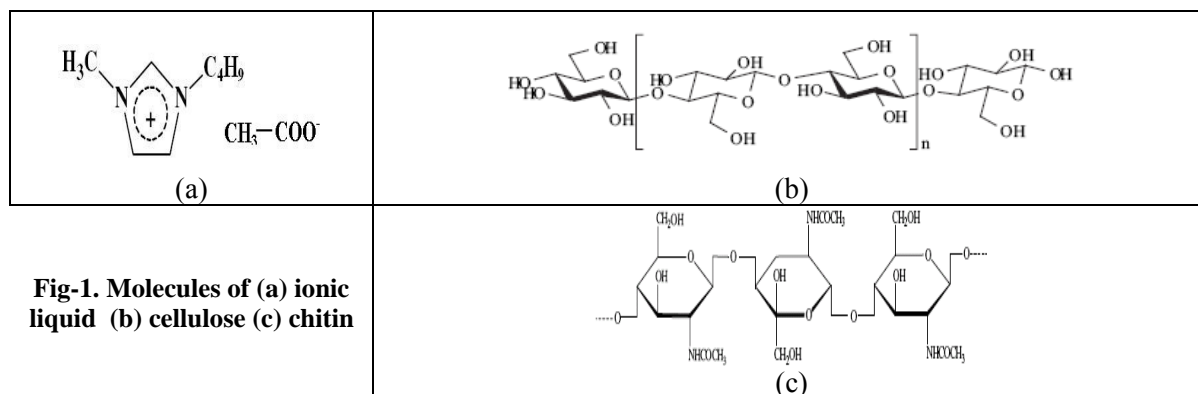


Fig-1. Molecules of (a) ionic liquid (b) cellulose (c) chitin

2 PRELIMINARY EXPERIMENTS

Preliminary experiments of solubility measurements have been done in order to select ranges of operating conditions for the regeneration process.

2.1 Solubility of cellulose and chitin in [BMIm]Ac

Cellulose DS-0 is purchased from Fluka, Chitin from USA Federal Laboratories, [BMIm]Ac from Solvionic SA (France) (melting mp < 20°C, density = 1020 kg.m⁻³) and ethanol from Fluka, (purity > 99.8 %).

The solubility is estimated by visual observation in a small stirred cell. Ionic liquid is introduced in the cell at controlled temperature and a known amount of solid is added progressively until an excess of solid is observed. After 2 hours, if the solid is not entirely dissolved it is assumed that the saturation has been reached. Should the dissolution be complete, the temperature is increased again and these steps are repeated.

The results are shown in Table 1. The solubility of the two polymers in [BMIm]Ac increases with temperature and reaches respectively 16.5 ± 0.5% (w/w) and 9 ± 1% (w/w) for cellulose and chitin at 70°C. [BMIm]Ac contained free acetate anions that disturb and break intra-molecular hydrogen bonds present in the both molecules (cellulose and chitin) making them soluble [8, 9, 10, 15]. The regeneration of solid from these solutions has been investigated.

Two solutions of ionic liquid/solute with weight fraction respectively equal to 16% for cellulose and 8% for chitin were prepared at 70°C. Then, the temperature was decreased from 70°C to 22°C by 10°C step. The mixture is observed during 2 hours for each level of temperature. The results show that the solution remains in the same state: no solid appears during the period of observation. The induction time for the regeneration of solid is higher than 2 hours probably because of the high viscosity of solutions.

Table-1. Measured apparent solubility of cellulose and chitin in [BMIm]Ac

Temperature [°C]	Solubility [%]	
	Cellulose	Chitin
22	3% soluble, 4% not soluble	<1%
30	5% soluble, 6% not soluble	0.5 soluble, 1.5% not soluble
40	6% soluble, 7% not soluble	1% soluble, 3% not soluble
50	9% soluble, 10% not soluble	4% soluble, 6% not soluble
60	11% soluble, 12% not soluble	6% soluble, 8% not soluble
70	16% soluble, 17% not soluble	8% soluble, 10% not soluble

2.2 Effect of CO₂ on the solubility

The effect of CO₂ on the solubility of the two polymers in [BMIm]Ac have been tested in a high pressure cell. Solutions of ionic liquid/solute near saturation at 16% and 8% (w/w) for cellulose and chitin respectively were prepared at 70°C. The two solutions were kept in an oven under vacuum at 26 KPa and at 70°C in order to remove the residual water in the cell.

In the cell the CO₂ was added to the solution of cellulose at 70°C by increasing the pressure. The solution was observed through a sapphire window during two hours for different pressures (5, 7, 10, 12, 15, 18, and 20 MPa): no

solid appears during the observation time. This simple experiment shows that CO₂ can not be used as an anti-solvent for the regeneration of cellulose.

The same procedure was used in the case of chitin. A formation of a gel is observed at low pressure (around 5 MPa). The stirring breaks the compact gel and small particles were observed. Changing the temperature (cooling or heating), this gel stays unmodified. CO₂ has a slight anti-solvent effect on the solubility of chitin in [BMIm]Ac, it can play an anti-solvent role and seems to promote the gelation process.

Chitin and cellulose have quite similar molecular structures. Therefore, more studies are needed to understand the reasons of these different behaviours.

3 RESULTS AND DISCUSSION

3.1 Generation of membranes in [BMIm]Ac

Solution of cellulose or chitin in ionic liquid at 5% (w/w) were prepared at 70°C. The solutions were poured in the moulds and let at room temperature and ambient humidity to allow the gel to form. Then the moulds were immersed in different anti-solvent: water at ambient temperature (22±1°C), hot water (70±1°C) and ethanol (22±1°C).

When the anti-solvent is cold, orange membranes were obtained (Fig-2). This colour is due to the presence of some ionic liquid in the membrane. By washing in the anti-solvent, this colour disappeared and yellow/white membranes were obtained in the case of chitin and white membrane in the case of cellulose (Fig-3). The formation of membrane is governed by the bidirectional diffusion: the anti-solvent enters into the membrane and the ionic liquid go outside.

With hot water (70°C), the orange colour disappeared more quickly. This phenomenon can be explained by the effect of the temperature on the molecular diffusion.

The membrane obtained with water immersion at ambient temperature appeared to be stronger than the membrane obtained in hot water. The increase of temperature accelerates the molecular diffusion and affects the polymer structure. The solute has not sufficient time to undergo strong rearrangement among the chains, so the structure is weak [7].



Fig-2. Polymer membranes after few minutes in water (22°C): (1) cellulose (2) chitin



Fig-3. Polymer membranes after 2 days in water (22°C): (1) cellulose (2) chitin

Ionic liquid can be extracted from the membrane by washing it with water or ethanol. Conductivity method based on the conductivity measurement in the water around the membrane has been tested in order to follow the extraction of the ionic liquid from the membrane.

An example of conductivity evolution during the washing is shown on Fig-4. A calibration curve giving the conductivity as a function of the ionic liquid concentration is used with the mass balance to estimate the residual amount of ionic liquid in the membrane at the end of the washing: around 90-95% of initial ionic liquid mass contained in the membrane was extracted by the washing.

3.2 Supercritical extraction

Membranes dried under vacuum at 45 °C were unstable: the colour of membranes changed as function of ageing time due to residual ionic liquid. So, supercritical extraction of residues from membranes has been tested in order to improve their stability by increasing the ionic liquid removal.

Membranes of chitin and cellulose were prepared using solutions of ionic liquid and solute at 5% (w/w) and water at ambient temperature (22°C) as anti-solvent. The membranes were washed with water for 48h and water was changed every day. After 48h, water was replaced by ethanol in order to test an easier way of supercritical extraction since ethanol is more miscible with CO₂ than water. The membranes were maintained in ethanol for 1 day.

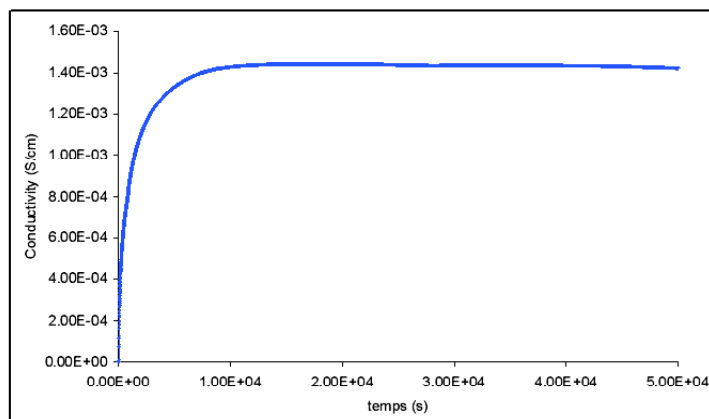


Fig-4. Conductivity as function of washing time

The membranes were put in an extraction cell (4) and undergo a supercritical extraction (Fig-5) using a Separex (France) extraction apparatus. Since the CO₂ is recycled in the process, it has to be separated from the water/ethanol extract, this separation being done after the back pressure regulator in the three cyclonic separators (5, 6, 7) in which the pressure decreases from 70 to 50 bars.

The operating conditions used in the process were:

CO₂ flow rate Q=5kg/h, P₄=16.8 MPa, P₅=7, P₆=6, P₇=5 MPa, temperatures T₄=T₃=45°C and T₅=T₆=T₇=40°C.

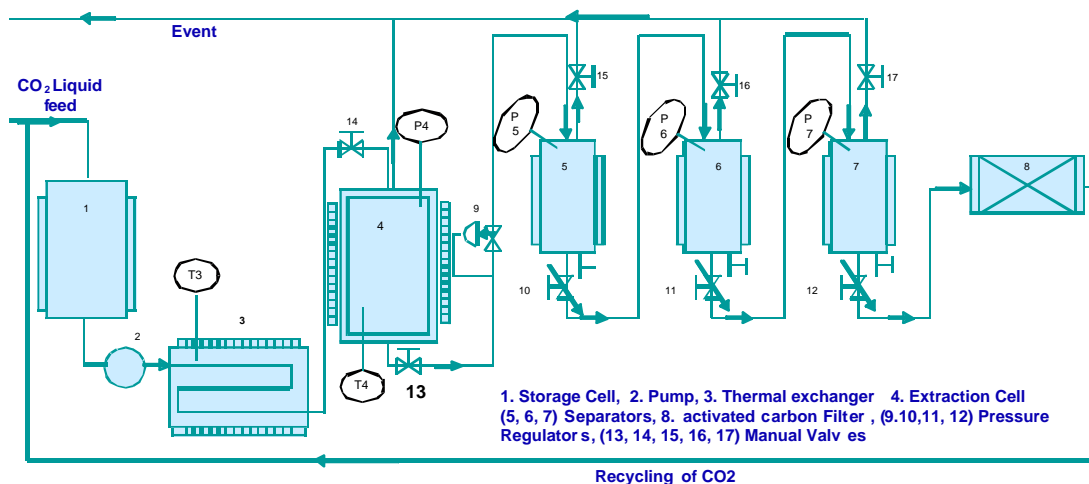
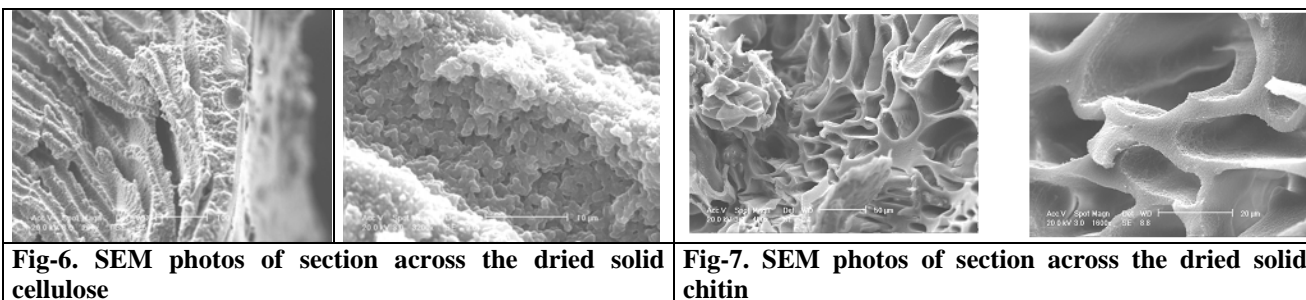


Fig-5. Supercritical drying process

Five membranes of cellulose and four membranes of chitins have been dried: a compact and porous solid was obtained. The colours of these solids are identical to their initial colours, that is: white for cellulose and white/yellow for chitin. These solids have been characterised by different techniques: Scanning Electronic Microscopy (SEM), Fourier Transform Infra Red Spectrophotometry (FTIR) and X-Ray diffraction.

Both of the solids exhibit porous structure (Fig-6, Fig-7). However, the chitin-based ones seem more porous than those of cellulose and the porous network is uniformly spread. The cellulose solid have a compact structure which is composed of superposed layers inducing the presence of some closed porosity.

The transmittance using InfraRed spectrometer of thin discs of membrane/KBr in ratio of (2/100 w/w) was measured. The cellulose spectrum (Fig-8) is similar to those in literature [9, 24]. Several peaks were observed: A large one at 3344.1 cm⁻¹ due to hydrogen bonds of the hydroxyl group, (2800-2900) cm⁻¹ assigned to stretching C-H, (1400-1500) cm⁻¹ assigned to oxymethyl group, (800-1200) cm⁻¹ assigned to valence vibration of C-O, C-C and external vibration of CH₂, COH, CCH, CCO, (400-800) cm⁻¹ assigned to vibrational spectra of cellulose. Compared to the dried cellulose solid, it can be seen that the spectra are quite similar except for the peak at 1578 cm⁻¹. This peak is also present in the chitin solid. This peak might therefore be assigned to the presence of residual ionic liquid in the solid.



X-Ray Diffraction analysis of initial cellulose confirmed that it was cellulose type I. The IR spectrum of the dried cellulose solid exhibits characteristic absorption of cellulose type II. The band at 1113 cm^{-1} is stronger in the initial cellulose and appears as a shoulder in the dried solid as result of the development of a strong band near 1067 cm^{-1} . The band at 894 cm^{-1} belongs to β -anomers or β -linked glucose polymers and the absorption peak in the dried solids becomes more intense and sharper than the corresponding one in initial cellulose. Zhang et al. found the same results with the regenerated cellulose [9]. It means that during the process, initial cellulose I is transformed to type II. This result indicates that some initial intermolecular hydrogen bonds are destroyed.

The IR spectra of chitin (Fig-9) remain similar to those found in several publications [25, 26, 27, 28]. Chitin presents three polymorphs α , β , and γ chitins. α and β chitins are the most abundant, they can be distinguished by infrared spectroscopy because of the different hydrogen bonds. The more obvious spectral difference is the frequency of the vibration modes of amide I in the region $1660\text{--}1620\text{ cm}^{-1}$. In the α -chitin two absorptions are observed at 1660 and 1627 cm^{-1} and in the β -chitin only one band at 1556 cm^{-1} [27, 28]. In the corresponding region of the OH and NH ($3600\text{--}3000\text{ cm}^{-1}$) groups the α -chitin exhibits a more detailed structure than that of the β -chitin. The comparison between our chitin spectra with the chitin spectrum of the literature shows that both the initial and processed chitins are of type beta. The spectra were used to calculate the chitin acetylated degree (DA) using the Moore and Roberts's method [29]:

$$DA = 100 \left(\frac{A_{1655}/A_{3450}}{1.33} \right)$$

Where, A_{1655} is the absorbance of amide I and A_{3450} is the absorbance of O-H stretching vibration.

For the initial chitin, we obtained the value of DA equal to 37%. After the process, the DA increases to 49%. So, new acetyl groups have been formed.

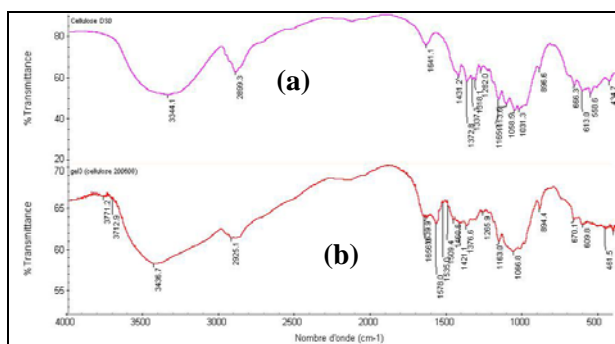


Fig-8. Infra red spectrum of (a) cellulose and (b) dried cellulose solid

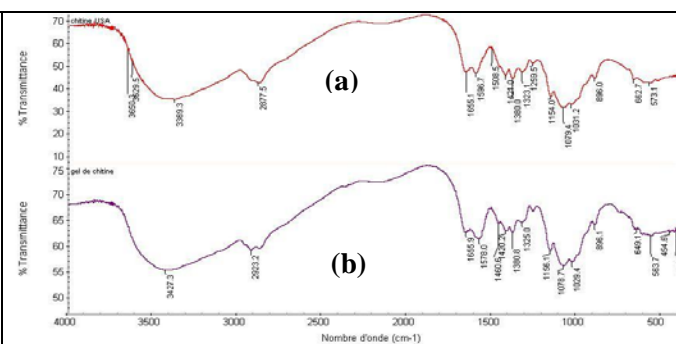


Fig-9. Infra red spectrum of (a) chitin and (b) dried chitin solid

4 CONCLUSION

The solubility of cellulose and chitin in [BMIm]Ac are high enough to develop new regeneration processes. For both solutes (cellulose and chitin), the dissolution seems to occur without any chemical reaction. Gels of chitin or cellulose were formed by cooling and contacting with ambient humidity.

Generation of membranes from gels was obtained by washing with water and ethanol. This process induces small structural modification in the polymer chains. The washing with water was monitored by conductivity. A soft and white solid was generated and most of the ionic liquid could be extracted during this operation. The overall material balance indicates that a range of 90-95% of the initial amount of ionic liquid was removed.

The supercritical CO₂ extraction tested on the membranes yielded to a porous and hard solid in which the water/ethanol residues were eliminated. Furthermore, most of the small residual quantities of the ionic liquid were also extracted.

On the whole, this supercritical extraction step permits to eliminate a quantity of ionic liquid larger than a simple drying under vacuum.

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