



Gas permeability properties of gelatin/polyetheramine blend membranes made without organic solvent



Jennifer Biscarat, Christophe Charmette, José Sanchez, Celine Pochat-Bohatier*

IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université Montpellier 2, Place E. Bataillon, F-34095 Montpellier, France

ARTICLE INFO

Article history:

Received 15 July 2014

Received in revised form 19 November 2014

Accepted 21 November 2014

Available online 18 December 2014

Keywords:

Blend membrane

Gas permeability

CO₂

Biopolymer

Polyetheramine

ABSTRACT

This study aims at developing bioartificial blend membranes using gelatin as the filmogenic agent and a green processing route. Two water-soluble, CO₂-phile, polyetheramine (PEA) synthetic polymers were added to gelatin to prepare the membranes. This present work focusses on the temperature effect on the gas permeability properties of PEA/gelatin blend membranes cross-linked with a non-toxic chemical (terephthalaldehyde – TPA). The permeability coefficients were related to the structural characteristics of the membranes. Increasing the gas flux temperature from 298 to 353 K raised the CO₂ permeability up to 19 times. CO₂, N₂ and He permeability increased steadily with diamine content while they showed an optimum for the triamine, with CO₂ permeability up to 250 Barrer, linked to the semi-crystalline nature of both gelatin and PEAs. The highest CO₂/N₂ selectivities were observed for the highest permeability values. Even if the overall selectivity values remains low for gas separation application, this work presents the study of the gas transport properties of alternative bio-based membranes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The manufacturing of membranes with synthetic polymer implies using large quantities of organic solvents which are generally toxic and costly to dispose of since they have to be eliminated from effluents. Developing gas separation membranes with bio-sourced polymers represents an alternative to petroleum-based material. These polymers become really interesting when they can be dissolved in water, avoiding the use of large quantities of organic solvents. As the large use of polymers from natural raw materials would require intensified farming of energy crops in competition with food production, material developments should be done now in direction of biopolymers coming from industrial by-products. Gelatin is an attractive choice since it represents a good equilibrium between human food consumption and valorization of industrial by-products. It is obtained by controlled hydrolysis of collagen, a fibrous insoluble protein, which is widely found in nature as the major constituent of skin, bones and connective tissue [29]. This biopolymer has been extensively used in the food and pharmaceutical industry for its gelling and texturing properties. However since the Bovine Spongiform Encephalopathy crisis and taking into consideration the religious usages, gelatin in Food Industry tends to be replaced by alginate or agar-agar.

Biopolymers have received a great attention for various membrane applications in the last decade. Chitosan was sorely studied for metal adsorption [33], pervaporation [54] and gas barrier [25,27]. Polyvinyl alcohol (PVA) is not a biopolymer since it is not bio-sourced, but it is often assimilated to biopolymers because of its hydro-solubility and biodegradability. PVA was used in blends with polysulfone or polyetherimide for gas separation [45,58,24], in blends with chitosan or gelatin for pervaporation application [46,52].

The main drawback of gas separation membranes from biopolymers is the low gas permeability of these materials which makes them incompatible with gas treatment processes but more attractive for packaging applications [41,5,16,26,8,47,56,20,42,43]. Gelatin gas transport properties were studied exclusively for oxygen and permeability values range from 10⁻⁴ to 10⁻² Barrer. Indeed, gelatin is a semi-crystalline polymer which crystallinity is consisting of the organization of protein chains in collagen like triple helices. This peculiar structure hinders the gas diffusion and makes gelatin a barrier material [10,11]. The phenomenon of folding/unfolding the triple helices is called renaturation/denaturation of gelatin.

One interesting way to improve the permeability fluxes is the addition of a second polymer, preferentially an elastomer. This will conduct to the obtaining of bioartificial blend membranes. Even if the addition of synthetic polymers reduces the “green concept” of gas separation membrane made only from biopolymers. One way

* Corresponding author. Tel.: +33 467 143 327.

E-mail address: Celine.Pochat@univ-montp2.fr (C. Pochat-Bohatier).

to keep as possible the environmental friendly character of the process is to avoid using organic solvents by adding hydrosoluble synthetic polymers.

Gelatin and low molecular weight polyetheramine (PEA) are water soluble; while this characteristic permits to develop a solvent free process, it could become a drawback if the membranes are in contact with water during their use. Thus the membranes have to be cross-linked. The most used cross-linker for gelatin is the glutaraldehyde, a highly reactive dialdehyde [15,9,17,36]. It reacts with the amine function of gelatin via several mechanisms [40]. Polyethylene oxide polymers (PEO) are known for their CO₂-phily [19,31,32]. PEAs have the same backbone functions than PEOs with amine terminal functions which make them cross-linkable by dialdehydes. However glutaraldehyde is a toxic compound [13], it was thus replaced by a non-volatile and innocuous dialdehyde, terephthalaldehyde (TPA). This compound is known to form imine via Schiff base reaction with the amine function of chitosan [21]. TPA can thus create cross-links between gelatin and gelatin, gelatin and PEA, PEA and PEA. Our group have studied the effects of cross-linking with TPA on gelatin membrane and have optimized the preparation of the cross-linked membrane [12].

This present work focusses on the effect of the temperature and formulation on the gas permeability of bioartificial PEA/gelatin blend membranes cross-linked with TPA and prepared without organic solvent.

2. Experimental

2.1. Materials

Gelatin (Type A, Bloom 188) was purchased from Sigma. Terephthalaldehyde (TPA, Aldrich) was used as cross-linker without further purification. Two polyether amine synthetic polymers (D600, T3000, Table 1) were kindly supplied by Huntsman Holland BV.

2.2. Preparation of membranes

Film-forming solutions were prepared by dissolving 20 wt-% gelatin powder in demineralized water at 60 °C, under stirring until complete dissolution. Bioartificial blend membranes were prepared by adding directly to the solution, D600 or T3000 at 0.4, 1 and 1.5 g/g of gelatin in gelatin solutions and then stirred at 60 °C for 1 h (see composition in Table 2). The cross-linking process was integrated in the formulation step. TPA (0.005 g/g of gelatin) was first dissolved in DMSO and then added to the gelatin/PEG or gelatin/PEA systems in solution at 50 °C and stirred for

1 h before casting, such as residual DMSO content in gelatin solution is less than 0.1%. Films were prepared by dry-casting of the gelatin solution at 30 °C on flat Teflon coated sheets thanks to a K Control Coater 101 (Erichsen Instruments). The solution was cast at 500 μm with an Erichsen Mod.411 0956 casting knife. Gelatin and blend films were allowed to dry at 20 °C under (45 ± 5)% relative humidity (RH) during 2 days. All membranes were stored at 20 °C in a box at 25 ± 5% RH before subsequent analysis.

2.3. Differential scanning calorimetry (DSC)

Thermal properties were determined on membranes at 45 ± 5% humidity. The membranes were analyzed using a differential scanning calorimeter DSC 2920 equipped with cooling accessory RCS90 (TA Instruments). The samples (≈6 mg) were sealed in aluminum TA pan. The instrument was calibrated with pure indium (T_m = 156.6 °C and ΔH_m = 28.3 kJ/kg) and used an empty pan as reference. Membranes were cooled from 25 °C to –40 °C and then heated up to 230 °C with a 100 °C/min heating rate. This high speed permitted a better peak resolution between the denaturation and the degradation endotherms and to determine glass transition temperature [34]. The renaturation level of gelatin was calculated from the denaturation endotherm following the method described by Achet et al. [1].

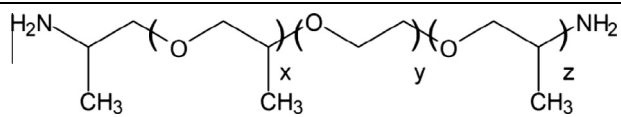
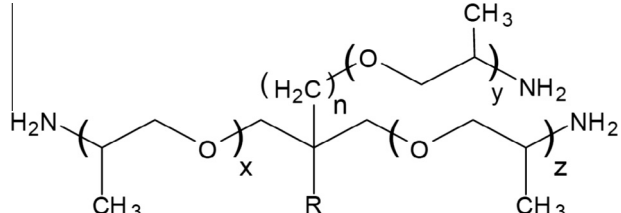
2.4. X-ray diffraction

The apparent crystallinity was determined by X-ray diffraction (PanAnalytical X'pert-Pro diffractometer). To eliminate the uncertainty due to the gelatin water content, the experiments were conducted in a sealed chamber (Anton Paar HT1200) after 15 h under vacuum, at room temperature. The crystallinity was determined considering the ratio between the area under the crystalline peak and the area under the amorphous halo following the method used by Charmette et al. [18]. Gelatin diffractogram shows two peaks: one about 7° and one between 17° and 22° representing respectively the triple-helical crystalline structure and the amorphous part of gelatin [57,48,2].

2.5. Gas permeation experiments

Permeation experiments were carried out by using the constant-volume and variable-pressure technique in a permeability apparatus at controlled temperature from 298 K to 353 K, described in the standard ASTM D 1434-82 (procedure V). The apparatus consists essentially of a two compartments permeation cell separated by the tested membrane. The permeability was obtained measuring the pressure increase in the downstream

Table 1
Formulae and molecular weight of the synthetic polymers.

Name	Formulae	Mw (g/mol)
D600		≈600
T3000		≈3000

Download English Version:

<https://daneshyari.com/en/article/640790>

Download Persian Version:

<https://daneshyari.com/article/640790>

[Daneshyari.com](https://daneshyari.com)