



Preparation and characterization of porous microfiltration membranes by using tailor-made propylene/1-octadecene copolymers

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Abstract

Tailor-made isotactic polypropylene (iPP) and propylene/1-octadecene (CiPP-OD) copolymers synthesized via a metallocene catalyst were used for membrane preparation by the thermally induced phase separation (TIPS) process. Although the resulting morphology of the membranes and porosity were found similar, the water permeability for propylene/1-octadecene copolymer membrane (1.0 mol-% of 1-octadecene) was twofold higher compared to iPP membranes. Further increase of 1-octadecene in the polypropylene did not improve the performance of membrane (decrease of permeability). This behaviour was attributed to the compressibility of the pores due to the ductile behaviour of the copolymer. Thus, the presence of a small amount of 1-octadecene (1.0 mol-%) in the polypropylene chain can lead to obtain membranes with improved water permeability for the microfiltration process.

Keywords: Polypropylene; Porous membrane; TIPS process; Microfiltration

1. Introduction

Polyolefins are known as commodity materials due to their great versatility and low cost [1–3].

Recently, great interest in the development of polypropylene and its copolymers with alpha-olefins has been noticed [4–7]. Polypropylenes synthesized via Ziegler–Natta catalysts (commercial) are isotactic, and they have a broad molecular weight distribution. On the other hand, those obtained via metallocene catalysts have a narrow molecular weight distribution and well-defined microstructure [1,4,5,8–11]. In the case

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of copolymers with alpha-olefins, the incorporation of the comonomer along the main chain is uniform, and it can be well controlled by polymerization conditions and comonomer concentration in the reactor [12].

Polypropylene is commercially used in the preparation of porous membrane via the thermally induced phase separation (TIPS) process. In the literature, many works about membrane preparation via the TIPS process by using commercial isotactic polypropylene can be found [18–26]. These membranes have potential application in the removal of bacteria, beer and wine clarification, waste water treatment, oil–water separation, blood oxygenation, etc. [13–17]. Nevertheless, the study of tailor-made polypropylenes for membranes can be considered important since a small change in the polypropylene microstructure can produce membranes with improved properties. In order to design a material for microfiltration membrane with improved performance, propylene/1-octadecene copolymers are synthesized via metallocene catalysts. The incorporation of 1-octadecene in the polypropylene main chain alters the polymer microstructure, and thus, its physical, thermal and mechanical properties are varied.

In order to control the pore size of the membranes, we studied different polypropylenes and we reported interesting results about the relationship between polymer microstructure, membrane morphology, and separation properties of different polypropylene membranes. Isotactic polypropylene (iPP) synthesized with metallocene catalysts produced membranes with larger pores than polypropylene membranes prepared from commercial iPP [27]. On the other hand, syndiotactic polypropylene (sPP) membranes presented deformed circular pores; these differences were attributed to the microstructure and physical characteristic of the polymers [28], and the gas and water permeability of sPP were lower than those of iPP membranes [29]. It was also reported that propylene/1-hexene copolymers (a

tailor made polypropylene) with controlled comonomer content can be used to prepare membranes with defined pore size [30].

In this work, a propylene/1-octadecene copolymer membrane with improved water permeability is presented. The improvement of the membrane performance was obtained by controlling the copolymer microstructure and comonomer content in the polypropylene.

2. Materials and methods

2.1. Materials

Isotactic polypropylene (iPP) and its copolymers with 1-octadecene (CiPP-OD) were used for membrane preparation. They have been synthesized via metallocene catalysts and characterized in our laboratory [12].

Diphenylether (DPE) was used without further purification as diluent for membrane preparation. Methanol (Aldrich) of technical grade was used for DPE extraction from the polymer matrix.

2.2. Methods

Comonomer content in the CiPP-OD copolymers was estimated from nuclear magnetic resonance (^{13}C -NMR) spectra. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC). Thermal properties were obtained by differential scanning calorimeter (DSC), and crystallinity of polymers was estimated from latent heat of melting.

The phase diagrams were obtained according to the previously reported method [27,28], and the TIPS process was used to prepare the membranes. This process has been introduced by Castro [18] and later it was described in many reports by Lloyd et al. [20–22,26]. Different polymers and diluent were prepared and mixed (13 wt-% of polymer) in a test tube; it was purged with nitrogen and sealed to prevent oxidation. In order to homogenize the solution, the test tube

was placed in the oven at 453 K for 48 h for iPP homopolymer and 24 h for CiPP-OD copolymer, and was then immersed in liquid nitrogen in order to induce fast solidification.

A small volume of the solid solution was taken and placed on a circular thin aluminum film mold (500 μm of thickness and 5 cm of diameter) and covered (sealed) with another thin plate. This system was placed in the oven at 453 K for 10 min, and it was then cooled by immersing in water at 293 K. The design and the material of mold should be suited to prepare membranes with isotropic structure. However, the temperature gradients through the thickness could lead to some anisotropy. The loss of diluent during this procedure was experimentally controlled, and it had been found to be <3 wt-% [29]. The extraction of DPE from obtained membranes was carried out with methanol, and in order to obtain good reproducibility, at least 2 membranes were selected from a series of prepared samples.

The membrane morphology was examined by scanning electron microscopy (SEM) using a TESLA BS343A instrument at an accelerating voltage of 15 kV.

Porosity was determined by gravimetric measurements of the difference between dry and fully isopropanol-filled membranes. The pore size was determined by using a permporometer (gas permeation, and liquid displacement) CFP-34RTG8A-X-6-L4 (PMI).

Water permeability of the membranes (sample area 4.9 cm^2) was measured in a pressure driven filtration cell with a magnetic stirrer (Amicon 8010, Millipore). Before measuring the water flow, membrane samples were carefully wetted with isopropanol followed by water.

The mechanical properties of the membranes were evaluated in a stress–strain test using an Instron Universal testing machine (Instron), calibrated according to standard procedures and equipped with a load cell and an integrated digital display that provided force determination. A load of 100 N and a strain rate of 0.67 min^{-1} were

used. The samples had 2.5 mm of width and the distance between the gags was 15 mm, and the presented values are the average of three samples.

3. Results and discussion

3.1. Polymer properties

In order to compare the membrane properties, polymers with similar average molecular weight and the same molecular weight distribution were synthesized (tailor-made polymers) [12].

Table 1 shows the molecular weight of all polymers. It has not been significantly influenced when the polymerization took place with an iso-selective catalyst, and for our purpose they can be considered the same. In a previous work Quijada et al. reported similar results, where propylene/1-octadecene copolymer was synthesized with different catalytic systems [4].

The melting and crystallization temperature (T_m and T_c) decreased when comonomer content was increased from 1.0 to 2.4 mol-% of 1-octadecene (Table 1) [4,31–33]. This decrease is mainly attributed to the percentage of introduced branches in the polymer main chain, which directly affected the size of crystallite. The presence of branches in the polymer chain would deteriorate the crystal structure, and thus, the melting and crystallization temperature, crystallinity and mechanical properties are affected as well.

3.2. Phase diagram

After synthesizing and characterizing the polymers, phase diagrams for different polymer-diphenylether systems were obtained, and Fig. 1 shows the phase diagrams for iPP-DPE and CiPP-OD-DPE, respectively. The obtaining of binodal (cloud point) and dynamical crystallization curve was carried out at a cooling rate of 10 K/min. The general characteristics and properties of a phase diagram can be found elsewhere [12,27], and these are not discussed in this work.

Table 1
Basic polymer properties

Material	Comonomer content (mol-%)	M_w^a (kg/mol)	T_m (K)	T_c (K)	Crystallinity (%)
iPP	—	310	425	385	44.0
CiPP-OD1.0	1.0	380	406	353	29.0
CiPP-OD2.4	2.4	350	384	333	17.0

^a $M_w/M_n = 1.8$.

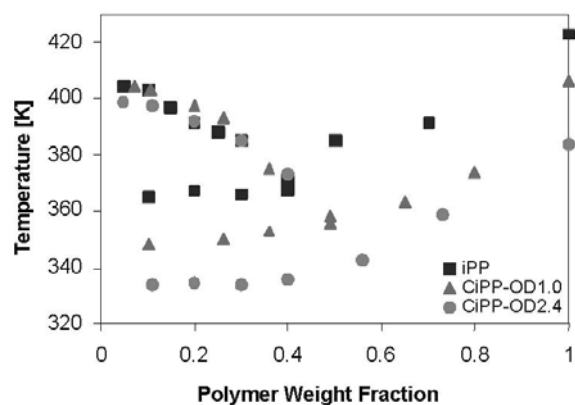


Fig. 1. Phase diagram for the iPP, CiPP-OD1.0 and CiPP-OD2.4 systems with DPE.

Although the phase diagram for iPP homopolymer and its copolymers with 1-octadecene with DPE (binary systems) present almost similar binodal line, the copolymer-diluent system has slightly shifted to higher temperatures than the homopolymer system. This small shift could be attributed to entropy effects during polymer solubilization [23,34] since the size of the comonomer would hinder the movement of the polymer.

The most important result (in the phase diagram) was the shift of the dynamic crystallization curve of CiPP-OD-DPE system to lower temperature than iPP-DPE. It can be attributed to the comonomer increase (1-octadecene) in the polypropylene chain. As seen above, it could be directly related to the polymer properties,

especially to the crystallization temperature of the copolymers (Table 1).

The shift of the dynamic crystallization curve is considered very important during membrane preparation, since the distance between binodal line and crystallization curve gives the growth period of the pores. Therefore, this is a determining factor during phase separation process which controls the final pore size [12,28,30].

3.3. Resulting morphology

All membrane samples were carefully prepared under the same conditions (TIPS process). Previous studies showed that the optimal polymer concentration for membrane preparation is 13-wt-% [12,29], which is because membranes with high porosity are obtained. Fig. 2 presents the resulting morphology of the membranes prepared from iPP and CiPP-OD copolymers. Figs. 2a, d and g show the surface morphology of different membranes, and Figs. 2b, e and h represent the cross section. Although the iPP membrane surface seems to be rougher than that in CiPP-OD membranes, all these structures can be considered similar.

In Fig. 2b, the micrograph reveals that the polypropylene homopolymer would have crystallized since it shows a grain-like spherulite structure. A magnification of this micrograph (Fig. 2c) shows spherical pores, indicating that the membrane was formed via liquid–liquid phase separation [35–38]. On the other hand, the micro-

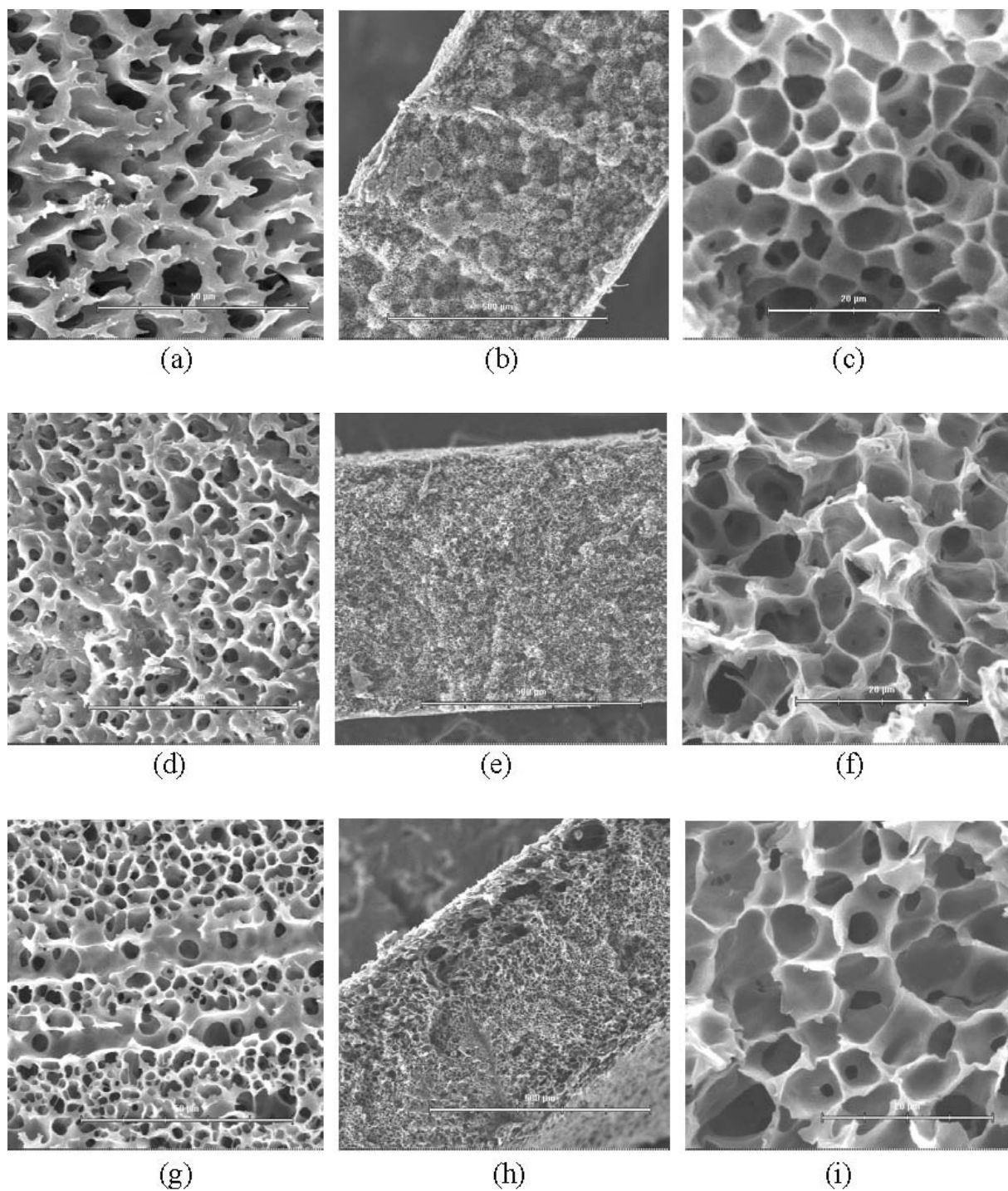


Fig. 2. Resulting morphology of different membranes: (a), (b) and (c): iPP; (d), (e) and (f): CiPP-OD1.0; (g), (h) and (i): CiPP-OD2.4. (a), (d) and (g): surface; (b), (e), (h): cross section overview; (c), (f), (i): detail of the inner part.

Table 2

Porosity, pore size and mechanical properties of the membranes; yield stress (σ_y), Young modulus (E) and strain at break (ϵ_r) as a function of comonomer content

Material	Comonomer content (mol-%)	Porosity (%)	Mean flow pore diameter (d) (μm)	σ_y (Mpa)	E (Mpa)	ϵ_r (%)
iPP	—	77	1.2	1.7	40	60
CiPP-OD1.0	1.0	79	1.0	1.5	15	200
CiPP-OD2.4	2.4	77	1.0	1.1	14	550

graphs in Figs. 2e and h, which represent copolymer membranes, do not show the formation of the spherulitic structure, which is due to the comonomer content (branches) that deteriorated the crystal structure of the polypropylene (Table 1). However, the pore structures are similar to that of the iPP membrane; thus the membrane formation in CiPP-OD membranes would have also been via liquid–liquid phase separation.

The observed macro-void defect in Fig. 2h is not a result of TIPS process. The CiPP-OD2.4 copolymer has higher ductile behaviour (Table 2) than the CiPP-OD1.0 copolymer and iPP homopolymer (as discussed below), and thus, this defect might be produced during sample preparation for SEM analysis because the fracturing of these samples was difficult and many pores could have been destroyed, producing macro-voids.

Pore structure in copolymer samples is not highly circular (compare Figs. 2c, f and i). This resulting structure can be attributed to a possible coalescence of pores during growth period; nevertheless, the quenching process (in water) would stop the pore growth, and thus, interconnected pores could be produced. McGuire et al. [39] have demonstrated that coarsening time lead to the merging of pores in membranes formed via TIPS process. As the phase diagram shows, the distance between binodal and crystallization curve in CiPP-OD systems increases, and therefore, the coarsening period could be increased. Thus, CiPP-OD1.0 and CiPP-OD2.4 membranes would present more interconnected

pores than iPP. This hypothesis is proven through the water permeability (the higher the pore interconnectivity, the higher the water permeability).

3.4. Porosity and permeability properties

For liquid transport, porous membranes are characterized in terms of flow and permeability properties [29]. According to the membrane morphology in this work, they could be used in microfiltration (MF) process. The membrane porosity for iPP and its copolymers based on gravimetric measurements was around 78% (Table 2), which was expected due to the initial polymer concentration (13 wt-%). This concentration is chosen in order to have liquid–liquid phase separation and high porosity [12,29]. Table 2 also shows the mean flow pore diameter (d), which represents the entire pore size distribution of the membranes determined by gas permeability [29]. These values can be considered similar, and are in agreement with the resulting morphology. However, it must be noted that the determined values may only provide a very rough approximation due to the significant deviations from cylindrical pore geometry.

Fig. 3 shows the average water permeability of different membranes (iPP and CiPP-OD). The permeability for the CiPP-OD1.0 copolymer membrane was twofold higher than that in the iPP homopolymer membrane. Nevertheless, an increase of comonomer (1-octadecene) content from 1.0 to 2.4 in the polypropylene unex-

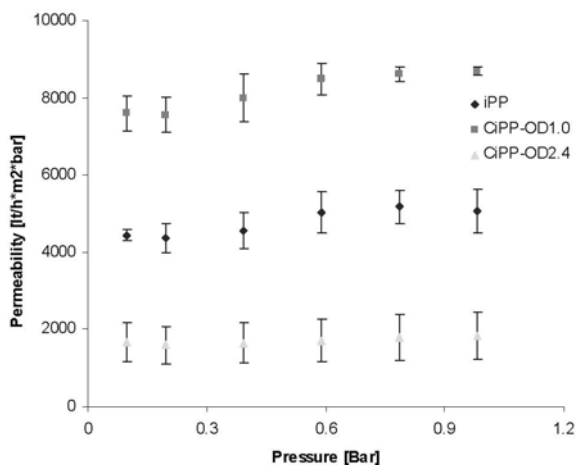


Fig. 3. Water permeability of iPP, CiPP-OD1.0 and CiPP-OD2.4 membranes.

pectedly decreased the permeability. The pore size, porosity and thickness ($600 \mu\text{m} \pm 5\%$ of error) were found similar; thus the permeability should be the same. An important factor which would have affected to the water permeability is the surface porosity and the pore compression during the flow process [29]. Although all samples were prepared in the same conditions, a difference in surface porosity could be expected. However, for a better understanding it should be studied with more detail. The pore compression could be due to the ductile behaviour of CiPP-OD2.4 copolymer because a mechanical test revealed a pronounced ductile behaviour for this copolymer (see Table 2). Yield stress (σ_y) and the Young modulus for copolymer samples decreased, and the strain at break for CiPP-OD2.4 sample was almost 10 times higher than iPP.

According to the hypothesis mentioned above (interconnectivity of pores); the water permeability for CiPP-OD1.0 fits with that (the higher the pore interconnectivity, the higher the water permeability). Therefore, the pore interconnectivity can explain the higher permeability in the CiPP-OD1.0 membrane since the membranes have the same porosity and same pore size. How-

ever, although the pores interconnectivity could be higher in the CiPP-OD2.4 membrane, the flexibility of this copolymer would have seriously affected the membrane performance (pore compression). Thus, copolymers with high content of 1-octadecene having high flexibility could not be used for microporous membranes.

Copolymers with higher amorphous phase and pronounced ductile behavior could have an interesting application for asymmetric membranes. The dense surface of the asymmetric membrane prepared from CiPP-OD2.4 copolymer would have higher gas permeability than other commercial and cheap polymers. Because these properties and low crystallinity of CiPP-OD2.4 samples, dense and asymmetric membranes are currently under investigation, and results will be reported soon.

4. Conclusions

Tailor-made polypropylene and propylene/1-octadecene copolymers with controlled and specific properties synthesized via metallocene catalyst were used for membrane preparation.

It was found that 1-octadecene content in the polypropylene chain affected the phase diagram, membrane morphology and water permeability. The dynamic crystallization curve in the copolymer systems (phase diagram) was shifted to lower temperature with respect to the iPP, which would have produced a coalescence of pores.

The resulting morphology of all membranes was similar. However, the pores would be more interconnected in CiPP-OD membranes due to the coalescence of pores during liquid–liquid phase separation. Although the membrane porosity was the same in all cases, the permeability of the CiPP-OD1.0 was twofold higher than the iPP membrane.

An unexpected decrease of permeability in the CiPP-OD2.4 membrane was observed, which could be attributed to the pore compression due to

the flexibility of this copolymer. Thus, it allows us to conclude that a small content of 1-octadecene (1 mol-%) in the polypropylene chain is sufficient to improve the water permeability.

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