



# Novel polypropylene-based microporous membranes via spherulitic deformation

K.-Y. Lin, M. Xanthos<sup>\*</sup>, K.K. Sirkar<sup>\*\*</sup>

Otto York Department of Chemical, Biological and Pharmaceutical Engineering, Center for Membrane Technologies, New Jersey Institute of Technology, Newark, NJ 07102, USA

## ARTICLE INFO

### Article history:

Received 18 June 2008

Received in revised form 12 December 2008

Accepted 29 December 2008

Available online 6 January 2009

### Keywords:

Melt processing

Spherulite

Solvent-resistant microporous membrane

Polypropylene

Nucleated polypropylene

## ABSTRACT

A novel method for creating a microporous membrane via spherulitic deformation is illustrated. The microporous structure was generated by the combination of intra-spherulitic and inter-spherulitic deformations. Polypropylene was selected due to its unique cross-hatched lamellar morphology facilitating inter-spherulitic deformation. A precursor film with a spherulitic structure was made under low-stress melt processing condition. A tangential lamellae-rich spherulite was created and identified with a positive birefringence sign. A sequential annealing process improved the crystalline structure, and in particular the thickness of the tangential lamellae. The annealing process proved to be critical for initiating the inter-spherulitic deformation. A WAXS examination provides a quick characterization method for the inter-spherulitic deformation. A highly interconnected solvent-resistant porous polypropylene membrane having a pore size in the range of 50–100 nm and a porosity of about 0.18 was thereby developed in this study. This concept can be further expanded by using an  $\alpha$ -nucleating agent to reduce spherulite sizes. A highly methanol permeable membrane with an estimated porosity of 0.29 was produced with the nucleated polypropylene samples.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Most polymeric membranes are made by the solvent casting process from polymer solutions. The porous structure of the membranes is created by phase separation induced through the addition of a non-solvent or by applying a temperature gradient. The characteristics of the porous structure, such as pore size and pore interconnectivity, depend on fine adjustments of the phase separation process [1]. Although the solvent casting process is able to create a variety of porous morphologies, it is limited in application vis-à-vis semicrystalline polymers. The tightly packed crystalline regions of semicrystalline polymers prevent their solvent dissolution and therefore limit their accessibility to the solvent casting process. As a result, these semicrystalline polymers are good candidates for making solvent-resistant membranes due to the presence of the crystalline domains.

Semicrystalline polymers, such as polyethylene (PE) and polypropylene (PP), cannot fully crystallize as a result of their high molecular weight and broad molecular weight distribution, even though their molecular structures are highly stereo-regular. An alternative method for creating porous structures in semicrystalline

polymers by the deformation of the crystalline structure has been established successfully since the 1970s under the trade name of “Celgard®” [2–4]. This stretching method, also known as the “dry process”, creates stacked crystalline domains by a melt extrusion process and creates pores by deforming them in a subsequent stretching process. When the polymer cools down from the molten state as it emerges from the extruder, nucleation leads to molecular chains packing and folding into lamellae. In general, these lamellae grow radially into spherulites. The spherulites keep growing until impinging other spherulites. Alternatively, the lamellae can form shish-kebab structures or stacked row lamellar structures by the interference of stress during crystallization [5], such as in fiber extrusion and in the “dry process”.

The “dry process” consists of three major steps: (1) extrusion, (2) annealing, and (3) stretching. In the first step, a desirable crystalline structure, the stacked row lamellar structure, is created in precursor films by utilizing high stress extrusion conditions such as low extrusion temperatures and high extrusion rates. The crystalline morphology of the stacked lamellae is further enhanced next by the annealing step. After that, the porous structure is created by deforming and separating these stacked row lamellae. The melt-processed membrane has small pore size (0.12  $\mu\text{m} \times 0.04 \mu\text{m}$ ) and narrow pore size distribution. It has good mechanical strength along the machine direction (MD) due to the “hard-elastic” nature of the stacked lamellae. However, the low tensile strength along the transverse direction (TD) may result in splitting problems during assembling of the membrane-based

<sup>\*</sup> Corresponding author. Tel.: +1 973 642 4762; fax: +1 973 596 8436.

<sup>\*\*</sup> Corresponding author. Tel.: +1 973 596 8447; fax: +1 973 642 4854.

E-mail addresses: [xanthos@njit.edu](mailto:xanthos@njit.edu) (M. Xanthos), [sirkar@adm.njit.edu](mailto:sirkar@adm.njit.edu), [kamalesh.k.sirkar@njit.edu](mailto:kamalesh.k.sirkar@njit.edu) (K.K. Sirkar).

devices [6]. The melt-processed membrane has been extensively used as a battery separator due to its solvent-resistance and good mechanical strength [7]. Nevertheless, there may be another way to utilize the crystalline structure to create a porous morphology. A novel strategy for preparing a porous membrane by using melt processing and deformation of the spherulitic crystalline structure is illustrated herein.

To date, there is no report on the use of the deformed spherulitic morphology as a basis for making a microporous membrane, even though the spherulitic structure has been studied for a long time. There may be a couple of reasons. First, compared to the stacked lamellar structure, the mechanical and morphological response of the spherulitic structure is more complicated due to the crystalline structure inherited from the choice of the processing conditions. Secondly, the positions of the broken lamellae openings are difficult to control.

Polymers show a ductile behavior when deformed above their glass transition temperature, and a brittle behavior below it. The lamellar separation can be intra-spherulitic or inter-spherulitic [8,9]. An intra-spherulitic deformation with a ductile response results in necking and cold drawing when the sample is stretched beyond the yield point. Then the sample can elongate up to several times its original length and form a highly oriented and tightly packed lamellar structure until the final structure breakdown occurs [10]. The locations of the lamellar separation cannot be controlled and neither the interconnectivity of these pores. Thus, it seems impossible to utilize these openings as manageable pores for membrane applications. However, there may be an opportunity to create useful microporous structures by combining this intra-spherulitic deformation with inter-spherulitic deformation.

The lamellae inside the spherulites are thicker and better compacted under slow crystallization conditions. Meanwhile, more non-crystallized impurities are rejected to the spherulite boundary, which makes it vulnerable under stress. As a result, the spherulites formed under slow crystallization conditions tend to deform inter-spherulitically [11]. The occurrence of inter-spherulitic deformation could compensate the stress which leads to catastrophic lamellar separation by intra-spherulitic deformation. Moreover, a good interconnectivity could be provided by the lamellar openings at the spherulite boundaries.

To demonstrate this concept, an important task is to find polymers with spherulites having strong lamellar structures to prevent catastrophic micronecking after the material yields. A choice among commodity semicrystalline polymers is isotactic polypropylene with an  $\alpha$ -form crystalline structure. Unlike other semicrystalline polymers whose lamellae always grow radially, the lamellae of  $\alpha$ -PP can grow in two directions, radially and tangentially. The cross-hatched pattern of radial lamellae (R-lamellae) and tangential lamellae (T-lamellae) is a unique pattern for  $\alpha$ -PP and has been documented in solution crystallization, bulk crystallization, and fiber spinning [12]. There are two important features of these T-lamellae relevant to this concept. First, the presence of T-lamellae improves the strength of spherulites by acting like “knots” and providing anchor spots when the spherulites deform. With the aid of this interlocking morphology, the  $\alpha$ -PP spherulites are more rigid and appear capable of maintaining their spherulitic morphology upon loading [9,13,14]. Secondly, the T-lamellae can act as extra space restraints during lamellar opening and this may lead to smaller pores [15]. The occurrence of inter-spherulitic deformation could be maximized by annealing. It is known that annealing improves crystallinity and enhances the perfection of crystals, and at the same time, non-crystalline impurities migrate to the spherulite boundary [16]. Both features could favor the occurrence of inter-spherulitic deformation.

The purpose of this study is to investigate the feasibility of creating porous structures via inter- and intra-spherulitic defor-

mations. Isotactic polypropylene is selected because of its unique cross-hatched lamellar structure. A parametric study of extrusion, annealing, and stretching conditions is reported. The concept is further expanded by utilizing nucleated polypropylene to reduce spherulite size. Finally, the novel porous membranes are characterized morphologically and the pore interconnectivity is examined via methanol permeability.

## 2. Experimental

### 2.1. Materials

A film extrusion grade polypropylene (PP), Dow H314-02Z, was used in this study. It is a homopolymer with a reported density of  $0.9\text{ g/cm}^3$  and MFR (melt flow rate) of  $2\text{ g}/10\text{ min}$ . A nucleated polypropylene (PPN), Dow H110-02N, with material properties similar to PP was also used in some experiments.

### 2.2. Membrane fabrication

#### 2.2.1. Step I: precursor film extrusion

The precursor films were extruded through a Brabender single screw extruder ( $D=1.8\text{ cm}$ ,  $L/D=15$ ) equipped with a 15-cm sheet die. The extrusion conditions were selected to ensure the formation of spherulitic structures instead of stacked row lamellar structures in the precursor films. The temperature setting of the extruder was  $230\text{ }^\circ\text{C}$ , the extrusion speed was 30 rpm, and the die-lip gap was fixed at  $100\text{ }\mu\text{m}$ . A three-layer take-up roll was used to collect the extruded film. The roll temperature was maintained at  $90\text{ }^\circ\text{C}$  by a circulating water bath. The distance between the extrusion die and the collecting roll was kept at 2.5 cm. The take-up speed was kept low to avoid generating additional orientation in the precursor films. The thickness of the precursor films was about  $70\text{ }\mu\text{m}$ .

#### 2.2.2. Step II: annealing

The precursor films were annealed in an air-circulating oven for 2 h. A long annealing time was selected to ensure that a steady temperature was reached. The annealing temperatures were set at  $100\text{ }^\circ\text{C}$ ,  $120\text{ }^\circ\text{C}$ , and  $140\text{ }^\circ\text{C}$ . The appearance and thermal analysis results of the annealed samples showed no signs of degradation. Samples designated as (An 100C), (An 120C), etc. indicate annealing at  $100\text{ }^\circ\text{C}$ ,  $120\text{ }^\circ\text{C}$ , etc.

#### 2.2.3. Step III: uniaxial stretching

A Tinius Olsen LOCAP universal testing machine equipped with a temperature control chamber was used for the stretching step. The non-annealed and annealed precursor films were cut as 7.6 cm wide rectangular sheets before stretching. The stretching direction was parallel to the extrusion direction, which is designated as the machine direction (MD). The films were held between two air-pressurized clamps with an initial distance between the clamps of 2.54 cm. The stretching rate was set at  $12.7\text{ cm}/\text{min}$ ; the films were stretched up to 7.6 cm (200% extension) at  $25\text{ }^\circ\text{C}$ . The stretched membranes were then held under tension at  $90\text{ }^\circ\text{C}$  for 10 min followed by cooling down to  $25\text{ }^\circ\text{C}$  for 20 min to stabilize the structure. The final membrane thickness was about 15–35  $\mu\text{m}$ .

### 2.3. Characterization

#### 2.3.1. Wide angle X-ray scattering (WAXS)

The wide angle X-ray scattering pattern of the films was recorded by a Philips PW3040 X-ray Diffractometer with a Cu  $K\alpha$  radiation ( $\lambda = 1.54\text{ \AA}$ ) and a  $2\theta$  range from  $10^\circ$  to  $24^\circ$ .

Download English Version:

<https://daneshyari.com/en/article/637189>

Download Persian Version:

<https://daneshyari.com/article/637189>

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