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Microporous Membranes Obtained from Polypropylene Blends with Superior Permeability Properties

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ABSTRACT: A blend of two polypropylene resins, different in molecular structure, one with linear chains and the other with long chain branches, was investigated to develop microporous membranes through melt extrusion (cast film process) followed by film stretching. The branched component significantly affected the row-nucleated lamellar crystalline structure in the precursor films. The arrangement and orientation of the crystalline and amorphous phases were examined by wide angle X-ray diffraction and Fourier transform infrared spectroscopy methods. It was found that blending of a small amount of a long chain branched polypropylene improved the orientation of the both crystalline and amorphous phases in the precursor films. Annealing, followed by cold and hot stretching were consequently employed to generate and enlarge pores in the films as a result of lamellae separation. SEM micrographs of the surface of the membranes obtained from the blend revealed elongated thin fibrils and a large number of lamellae. The lamellae thickness for the blend was much shorter in comparison to that of the linear PP precursor film. The permeability of the samples to water vapor and N₂ was significantly enhanced (more than twice) for the blend system. The porosity of the blend membrane showed a significant improvement with a value of 53% compared to 41% for the linear PP membrane. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 46: 148–157, 2008

Keywords: branched PP; linear PP; membranes; polypropylene blends

INTRODUCTION

Polymer membranes are increasingly employed for separation processes. They are relatively economic and cover a broad range of applications from microfiltration to reverse osmosis. The most common method for the fabrication of polymer membranes is based on solution casting followed by phase separation, process for which solvent contamination and costly solvent recovery are two major drawbacks.¹ One technique, which is applicable to semicrystalline polymers,

is based on the stretching of a thin film with a row nucleated lamellar structure.² In this case, pores are created as a result of lamellae separation. This method is relatively less expensive and there is no solvent contamination. The major disadvantage for this technique is the low tear resistance of the membrane in the machine direction (MD) that is due to the highly oriented crystalline structure.

The fabrication of membranes by stretching is carried out in three main consecutive stages: (1) production of the precursor film with a lamellar morphology, (2) annealing of the film to make the lamellae thicker and uniform, and (3) stretching of the film at low temperature to create voids and then at high temperature to enlarge the

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pores.^{2,3} One of the main issues in this process is the generation of a proper initial row nucleated structure. The polymer type and extrusion conditions are key factors for this matter.³ These factors determine the type, orientation, and position of crystal blocks in precursor films. Annealing will, in turn, partially remove the defects in the crystalline phase and make the lamellae more uniform. Consequently cold and hot stretching generate and enlarge the pores and determine the configuration and properties of the obtained membrane. The parameters controlling the final membrane structure can be classified into material and process categories.

Material parameters mainly include molecular weight and chain structure of the polymer. Adding a small amount of a long branched polypropylene into a linear PP generates a network with larger chain entanglement density in the melt state. Branched PPs are mostly used for foam applications because of their high melt strength.^{4,5} Branched PPs give a better foam structure through an improvement of the microbubble stability inside the melt phase.⁴ A stronger network formed as a result of larger entanglement density in the melt state relatively reduces the probability of bubble rupture and coalescence. The effect of blending of a branched PP with a linear PP on the melt rheological properties have been already studied.⁶ The important impact is reflected in the strain hardening behavior of the melt in elongational flow. The branched component form a molecular tree-like structure in the melt state that entangles with linear chains and results in a strain hardening behavior upon stretching.⁶

Agarwal et al.⁷ have investigated the effect of PP branching on the shear induced crystallization process. Increasing the branching level improved the orientation and mechanical properties such as the flexural modulus and the tensile yield strength in crystallized PP samples. They attributed the strong crystal orientation and improved crystallization kinetics in flow to the unique molecular architecture of the long chain branched polypropylene chains and the related effect on their broadened and complex relaxation behavior.

In our previous investigations, we have studied the material and process conditions for the production of microporous membranes from linear polypropylene resins.^{8,9} We have shown that the molecular weight and the molecular weight distribution control the crystalline structure of the pre-

cursor PP film, which in turn determine the final microporous structure of the membrane. In this work we investigate a novel formulation of a blend based on a branched and a linear PP resin with the objective of developing microporous membranes with superior permeability properties.

EXPERIMENTAL

Materials

The two polypropylene grades used in this study are homopolymers: Pro-fax 814 that is a branched polypropylene having long chain branches with a MFR (230 °C/2.16 kg) of 2.8 and PP4612E2 that is an ExxonMobil grade used for the production of oriented films with a MFR of 2.8. Fourier transform infrared spectroscopy (FTIR) tests carried out on both resins showed no trace of ethylene in their absorption spectrum. These resins are designated as PPB and PP28, respectively in this article.

Blending

Blending of the PP resins was carried out using a Leistritz corotating twin screw extruder, $D = 30$ mm and $L/D = 40$, equipped with two mixing zones composed of kneading blocks with $L/D = 4$. The screw speed was held at 100 rpm and the extruded material was pelletized after passing through a water bath at room temperature. The temperature of blending was set at 200 °C.

Rheological Characterization

The linear viscoelastic data and relaxation spectrum of both polymers can be found in refs. 3 and 8. The extensional behavior of the resins and blends was determined using an ARES rheometer (Rheometric Scientific), equipped with the new SER universal testing platform from Xpansion Instruments. The model used in our experiment was SER-HV-A01, which is a dual windup extensional rheometer and has been specifically designed for the ARES rheometer platform. It is capable of generating elongational rates up to 20 s^{-1} under controlled temperature (up to 250 °C).

Film Preparation

The films were prepared by cast film processing with a slit die at the temperature of 220 °C. To

improve cooling, a fan was installed to supply air to the film surface right at the exit of the die. The slit die dimensions were: width = 180 mm and lip gap = 1.9 mm. The key parameters were the fan speed, take-up roll speed and die temperature. We used the maximum speed of the fan, constant die temperature (220 °C), and constant extrudate flow rate of 1 kg/h the only variable was the take-up speed. Since the extrudate velocity at the exit of the die was constant the take-up speed determined the draw ratio for the film production.

Membrane Preparation

Membranes were produced by the stretching of the annealed precursor films to 40% (in cold stretching: room temperature) and another 40% (in hot stretching: 140 °C), both with respect to the initial length.

Film and Membrane Characterization

Crystal orientation measurements were carried out using a Bruker AXS X-ray goniometer equipped with a Hi-STAR two-dimensional area detector. The generator was set up at 40 kV and 40 mA and the copper CuK_α radiation ($\lambda = 0.1542$ nm) was selected using a graphite crystal monochromator. The sample to detector distance was fixed at 80 mm. Prior to measurements, careful sample preparation was required to get the maximum diffraction intensity. This consisted in stacking several film layers in order to obtain an optimum total thickness of about 2.5 mm.

Tensile tests were performed using an Instron 5500R machine equipped with a chamber for running tests at high temperature. The procedure used was based on the D638-02a ASTM standard.

For FTIR measurements, infrared spectra were recorded on a Nicolet Magna 860 FTIR instrument from Thermo Electron Corp. (DTGS detector, resolution 4 cm^{-1} , accumulation of 128 scans). The beam was polarized by means of a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp. The crystalline and amorphous orientations were measured based on the method that has been explained in detail in ref. 3.

The DSC (differential scanning calorimetry) tests were carried out on a TA Instruments Q1000 with the heating rate of 20 °C/min.

Permeability of water vapor was measured via a MOCON PERMATRAN-W Model 101K at room temperature. For nitrogen the flow of gas transmitted through the membrane was measured with a photo flowmeter (Optiflow520). The set-up for nitrogen permeability was built in our lab.

The pore size distribution and porosity were evaluated using a mercury porosimeter (Pore Sizer 9320-Micromeritics).

RESULTS AND DISCUSSION

Extrusion and Materials

The first step of this work was to add a small amount of a branched PP into a linear PP in order to create a particular lamellar crystalline structure for the films obtained from cast extrusion. Initially the preparation of a proper blend based on the dispersion of the branched polypropylene into the linear matrix was a major concern. The melt blend system of the two polyolefins usually show a LCST (lower critical solution temperature) behavior;¹⁰ hence, the favorite conditions for obtaining a miscible system will be the use of a small fraction of PPB and low blending temperature. Efficient mixing zones are also needed for the screw configuration to accelerate the dispersion.

To verify the miscibility of the blend system, frequency sweep tests were performed on the samples in the linear viscoelastic domain, and the agreement with the log additivity rule for the blend was examined.¹⁰ In addition to that, any immiscibility (or partial miscibility) in the melt could be tracked in solid thin film stretching, where it will result in nonuniform voids distribution and whitening throughout the film. Figure 1 reports the frequency sweep data for the two PP samples and the 40% blend.

A good agreement between the measured viscosity of the blend and that obtained from the log-additivity rule is observed, which is indicative of miscibility of the blend system from thermodynamic point of view. To improve the kinetics of the dispersion, mixing zones need to be effective, but at the same time not too aggressive to avoid degradation of the materials. The degree of degradation during extrusion was quantified by the change in the complex viscosity of molten samples of the precursor films and a reduction by less than 5% was considered to

Figure 1. Complex viscosity in small amplitude oscillatory shear for the resins at 230 °C.

be acceptable. The temperature for the mixing zones in extruder was set at 200 °C; however, for the die lip the temperature was increased to 220 °C to improve the quality of melt during stretching at the die exit.

Permeability tests for the final microporous membranes produced from the blend with different proportions of PPB revealed that exceeding the amount of 2% PPB did not considerably improve the permeability. In fact, it adversely affected the mechanical properties of the films.

Melt elongational tests were carried out for the samples under two Hencky strain rates and two different proportions of PPB (2 and 10%) and the results are reported in Figure 2. Adding PPB improves the melt strength that is evidenced by the strain hardening behavior of the melts. It is observed that strain hardening for

Figure 2. Transient elongational viscosity of the blend samples at 200 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3. Stress–strain obtained from the elongational tests at the elongational rate of 5 s^{−1} and 200 °C.

low content of PPB (2%) is only pronounced when the Hencky strain rate is large enough (around 5 s^{−1}, that is similar to the real strain rate applied at the die during cast film extrusion). For larger PPB content blends, such as 10%, strain hardening is observed under both low and high Hencky strain rates. It is also important to note that strain hardening occurs at shorter strains and is more pronounced for larger strain rates. Similar trend for such system has been observed elsewhere.¹¹

To show the effect of adding PPB on the improvement of the melt strength of the blend in a better way, stress versus strain for the melt state, extracted from the elongational data (for 2% PPB and Hencky strain of 5 s^{−1}) and plotted in Figure 3. As it can be seen, the blend system could sustain higher stress in comparison to PP28 for the same range of applied strain.

In the precursor films produced by cast film extrusion, the orientation and arrangement of the crystal lamellae are key factors in controlling the final structure of the obtained membrane. To reveal this effect, wide angle X-ray diffraction (WAXD) measurements were carried out and Figure 4 reports the diffraction patterns for the film samples. The first and second rings represent the patterns for the 110 and 040 crystalline planes, respectively.¹² The normal to the 110 plane is the bisector of the *a* and *b* axes and 040 is along the normal of the *b*-axis of unit crystal cells, as shown in the sketch of Figure 4(d). The arcs are sharper and more concentrated in the center for the blend sample that is indicative of greater orientation of the crystal lamellae.¹²

Figure 4. WAXD spectra for the precursor films (a) PP28 for a draw ratio of 48, (b) Blend of 2% PPB with PP28 for the same draw ratio, (c,d) crystal block and film production coordinates, respectively.

The pole figure results obtained from the integration of the 2D diffraction spectrum could be employed to calculate the orientation functions. Table 1 reports the orientation functions of the crystal unit axes with respect to the fixed coordinate in the MD. Adding 2% of PPB into PP28 promotes the orientation of the c -axis along MD and push the b -axis from ND (normal direction) towards the ND-TD (transverse) plane. The enhancement in orientation is attributed to the larger amount of initial fibrils formed at the nucleation stage of crystallization for the blend, resulting in a more oriented network.

The orientation of the amorphous and crystalline phases (c -axis with respect to MD) of the samples has also been measured by FTIR and

the results are presented in Table 2. The orientation function was calculated as:¹³

$$f_{i,MD} = \left(\frac{D - 1}{D + 2} \right) \quad (1)$$

where D is the ratio of the absorbance in the machine (parallel) to that in the transverse direction (TD). For the orientation function of the crystal phase (c -axis with respect to MD), f_c , the band 998 cm^{-1} is considered so D will be $(A_{\parallel}/A_{\perp})_{998}$, where A is the absorbance. To measure the total orientation that includes both the crystalline and the amorphous phase orientations the band at 972 cm^{-1} was selected and f_{av} (average orientation) was calculated based on

Table 1. Orientation Functions of Crystal Lamellae with Respect to the Production Coordinates (MD, TD, and ND)

PP28-DR = 48	f'_a	f_b	f_c	2% Blend-DR = 48	f'_a	f_b	f_c
MD	0.01	-0.45	0.44	MD	0.0	-0.47	0.47
TD	0.03	0.19	-0.22	TD	-0.02	0.27	-0.25
ND	-0.03	0.27	-0.24	ND	0.02	0.2	-0.22

Table 2. Orientation of the Crystalline and Amorphous Phases of the Precursor Films for the Initial Draw Ratio of 48

Sample	f_c	f_{av}	f_{amor}
PP28	0.48	0.35	0.26
PP28-An	0.57	0.42	0.33
2% Blend-An	0.61	0.45	0.34

$(A_{11}/A_{\perp})_{972}$. Assuming that the degree of crystallinity of the film is almost constant, the orientation of the amorphous phase, f_a , can be determined from these two values by:

$$f_{av} = X_c f_c + (1 - X_c) f_a \quad (2)$$

where X_c is the degree of crystallinity and was calculated based on DSC results. As it is observed in Table 2, the orientation for both crystalline and amorphous phases is increased in the precursor films of the blend. The increase in the orientation as stated previously is attributed to the formation of a particular crystalline structure for the blend. The larger entanglement density for the blend system increases the number and the rate of formation of initial base fibrils nuclei in the early stage of stress induced crystallization. We have already shown that the c -axis crystal orientation measured by FTIR is in reasonable agreement with the values obtained from the WAXD results.³

As the melt film is stretched at the die exit, the presence of branched PP chains forms a larger number of entanglements that result in a quick generation of elongated nuclei sites. The increase in the amount of initial elongated nuclei sites causes more lamellae to be generated with a relatively smaller thickness, as sketched in Figure 5.

The results of DSC experiments for the precursor films ($DR = 56$) are presented in Figure 6. PP28 showed a higher melting peak due to its larger molecular weight. The addition of 2% PPB does not affect significantly the trend of the curve; however, the position of the peak maxima for the blend shifts slightly to lower value as expected as a result of formation of lamellae with smaller thickness. The shoulder of the peak also becomes more noticeable, indicating two types of crystal blocks.

Tensile tests were carried out on the precursor films (prepared with initial $DR = 56$) to examine the response of the crystalline structure to stretching. The thickness of the samples was 25 μm and the reproducibility error for tensile tests was less than 4%. The first impact of blending PPB is a reduction of the elongation at break. As depicted in Figure 7, the trend of the curves for the blends remains the same with no significant changes up to 5% of the PPB resin. For larger contents of PPB, a drop in the tensile force is clearly observed. Incorporating a larger amount of PPB, which is estimated to have a lower molecular weight as indicated by the lower plateau in Figure 1 (and also explained in ref. 8), likely induces smaller density of the tie chains for the crystalline structure. A direct relationship between the mechanical properties and the fraction of tie chains has been assumed by Nitta and Takayanagi.¹⁴ In addition to that, above 10% of PPB, the possibility of immiscibility for the system is increasing. One or both of these factors cause the drop in the tensile properties.

After production of the precursor films, annealing was performed to homogenize the lamellar structure and improve the orientation of the crystal blocks.¹⁵ Figure 8 shows the effect of annealing on the responses to stretch-recovery tests. As shown in our previous article⁹ anneal-

Figure 5. Schematic of predicted lamellar structures: (left) linear and right (blend) PP film.

Figure 6. DSC of the PP28 and 2% blend samples (heating rate of 20 °C/min). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing has a significant impact on the stress–strain behavior. In simple words, it removes the defects from the crystalline phase and rearranges the crystalline lamellae in a more uniform way. This is one of the main reasons for the change in behavior between the two. For the case here, blending 2% of the branched PP has slightly improved the elastic recovery of the annealed film compared to the unblended linear PP. The tensile properties of the nonannealed film are also shown for comparison. The mechanical strength for the 2% blend in the applied range of strain is also slightly improved and that might be the result of a better orientation of the crystal blocks. As explained above, adding 2% of

Figure 7. Tensile properties of the precursor films samples produced with initial draw ratio of 56, stretching speed was 100 mm/min (at room temperature). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8. Tensile properties of the precursor films produced under a DR of 56; the stretching and recovering were performed at a speed of 100 mm/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PPB changes the crystalline structure of the linear PP through the formation of a larger amount of elongated fibrils with a larger number of thin lamellae grown on them.

Cold and Hot Stretching

The annealed samples were cold stretched up to 40% of the initial length at 25°C inside a chamber then heated up to 140 °C for 20 min to be hot stretched to another 40% to obtain the final membrane. As explained in our previous work,⁸ the following phenomena take place simultaneously during cold stretching such as: (1) voids formation as a result of chain scission of short tie chains, (2) slippage of crystal blocks and their reorientation along the stretching direction, (3) stretching of longer tie chains as shorter tie chains are broken apart, and (4) crystallization of highly stretched long tie chains. Depending on the initial processing conditions for the precursor films and stretching conditions, the relative contributions of each of these phenomena during stretching differ. Figure 9(a,b) present SEM micrographs of the final membranes after cold and hot stretching for the linear PP and the 2% blend, respectively. For the blend, long elongated fibrils are clearly observed with a length of over 3 μm and thin lamellae are formed on them. In contrast for the precursor film of the linear PP, thicker lamellae with much less pores between them are observed. It is speculated that such long fibrils for the blend could be formed during the hot

Figure 9. SEM micrographs of the surface of microporous membranes. Left PP28 (a) and right 2% blend (b) for initial DR = 56, The final membranes thickness was 22 μm and scale bar on the micrographs is 1 μm .

stretching as short elongated fibrils join together (because of larger mobility and slippage) and recrystallize in the stretching direction to create a much longer fibril network.

Table 3 reports the water vapor permeability for the membranes. The values are also compared to that of a commercial microporous Celgard membrane. The permeability for the blend membrane is more than twice that of the linear PP membrane and comparable to that of the commercial Celgard membrane. This is most probably due to the larger amount of the interconnected pores as a result of better orientation and thinner crystalline lamellae for the precursor film of the blend.

Depending on the application, membranes are often used under pressure. The evaluation of their performance in those conditions is reproduced by subjecting the membranes to N_2 gas flow under pressure. The results obtained for the permeability in terms of the gas flow rate versus pressure are presented in Figure 10 for PP28 and the 2% blend. The tested membranes

were cut by a circular punch having a diameter of 47 mm. Significant enhancement in the flow rate is observed for the blend system, as the flow rate jumps to much larger values under the same applied pressure. Another clearly observable result is the disappearance of the transition from the Knudsen diffusion regime to the Poiseuille flow, which for the linear PP sample was found to be around a pressure of $0.35 \times 10^5 \text{ Pa}$.⁹ In membranes with smaller pores and more narrow interconnected channels the permeability is controlled by the Knudsen diffusion. In membranes with larger pores and larger interconnected channels, the pressure gradient controls the permeability as the molecules are smaller than the pores and flow more freely through the channels.

Mercury Porosimetry

The porosity and pore size distribution from mercury porosimetry are reported in Figure 11 for two microporous membranes produced from initial precursor films under a draw ratio of 56. For the linear PP a peak in the pore size distribution around 0.10 μm is observed, whereas for the blend membrane, the whole curve is shifted to higher values with a peak around 0.15 μm . The porosity was evaluated as 41 and 53% for the linear PP and the blend membranes, respectively. The intrusion volume of mercury is directly related to the pore size and porosity due to interconnected pores. Lower effective pore size for the linear PP is attributed to thicker lamellae in the precursor film with lower orien-

Table 3. Vapor Water Permeability of Membranes Produced from Precursor Films Under an Initial Draw Ratio of 56

Sample	Permeability ($\text{g}/\text{m}^2 \cdot \text{day}$) (Error: $\pm 5\%$)
PP28	19,350
2% Blend	42,500
Celgard 2400	41,700

Figure 10. Flow rate of nitrogen versus applied pressure for two (PP28 and 2% blend) membranes produced from precursor films under an initial draw ratio of 56. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tation resulting in a difficult lamellae separation and less interconnectivity.

One major problem of such microporous membranes, as mentioned in the introduction, is the very low tensile strength in the TD. Usually, orientation improvement of the precursor films in MD sacrifices the strength properties in TD. The low strength in TD as shown in Figure 12 proves that fibrils do not form a unit bulk crystal. Apparently, a low van der Waals force between the untied fibrils causes a very easy failure of the film upon stretching in TD. The tests were performed with a load cell of 10 N to

Figure 11. Pore size distribution for two (PP28 and 2% blend) membranes produced from initial precursor films under a draw ratio equal to 56. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 12. Tensile properties in TD for two (PP28 and 2% blend) membranes produced from initial precursor films under a draw ratio equal to 56. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

enhance the accuracy of the results. It is observed that despite the orientation improvement in MD, blending promotes the strength in TD as well. We again attribute this to the particular structure formed in the blend system. For the linear sample, there are less elongated fibrils and a lower stress is needed to break apart the fibril units.

CONCLUSIONS

In this work we have investigated the properties of porous membranes obtained from blends of a branched and linear PP. Adding a small amount of a branched PP into a linear PP significantly increased the amount of entanglements in the melt state resulting in strain hardening. The early formation of entanglements during melt stretching created a specific crystalline structure for the blend upon crystallization in the precursor film, which favored orientation of the crystals blocks and also improved the tensile strength in the machine direction. The long elongated fibrils with thinner lamellae grown based on them were observed for this specific structure. The larger amount of pores and porosity are the result of such structure developed under stretching. The larger pores formed for the blend improves the permeability of the membranes. The blend membrane showed a major enhancement in the permeability to N₂ under pressure and the transition of the Knudsen regime to the Poiseuille flow disappeared. The highly permeable blend membrane had pores

around 0.15 μm and porosity of 53%, whereas the linear PP membrane had smaller pores of 0.10 μm and a porosity of 41%. The mechanical strength in TD for the blend membrane showed an improvement despite the increase of orientation in MD.

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