

# MICROPOROUS MEMBRANES BY MELT PROCESSING OF POLYPROPYLENE BLENDS

*M. Xanthos, C. Chandavas, K. K Sirkar and C. G. Gogos*  
*Department of Chemical Engineering and Polymer Processing Institute*  
*New Jersey Institute of Technology*  
*Newark, NJ 07102, USA*

## **Abstract**

Novel microporous membranes with pore size ranging from 2 to 25 nm were produced from immiscible polypropylene blends via melt processing and post-extrusion treatments. Systems containing polystyrene and polyethylene terephthalate as the minor phase components and optional compatibilizers were employed as starting membrane materials at concentrations not exceeding 15% by wt. The blends were first compounded in a corotating twin-screw extruder and subsequently extruded through a sheet die to obtain the non-porous precursor films. These were drawn (100-500%) with respect to the original dimensions at a temperature below the glass transition temperature of the minor phase to induce a microporous structure and then post-treated at elevated temperatures to stabilize the porous structure, which consisted of uniform microcracks in the order of a few nanometers in width. The effects of blend composition and extrusion process parameters on surface and cross-sectional porosity and solvent permeability of the prepared films are presented and related to specific microstructural features of the films before and after drawing. Finite element modeling of the stretching operation in the solid state yielded a successful interpretation of the blend response to uniaxial tension that resulted in microcrack formation. The processes developed in this work may be considered as solventless alternatives to phase inversion-manufacturing practices for membranes containing mesopores. Comparison of some of the novel microporous structures with commercial membranes prepared by solvent-based phase inversion processes suggests comparable pore size and porosity ranges, with narrower pore size distribution.

## **Introduction**

Microporous polymeric membranes are conventionally produced by phase inversion processes that use solvents to dissolve, usually, amorphous polymers. Homopolymers having much higher solvent resistance e.g. polypropylene, polyethylene have been employed to produce porous/microporous membranes via melt processing and post-extrusion treatments. However, this technique has been successfully employed only for a few semicrystalline polymers. (1-4) An objective of the present research is to provide a novel and general strategy for forming porous/microporous membranes by using immiscible polymer blends via melt processing and post- extrusion treatments. Such films having pore size and distribution as well as porosity comparable to phase inversion membranes could be used for various separations such as ultrafiltration, battery separators, etc.

## **Fabrication Procedure**

Systems containing components with different rheological characteristics consisted of polypropylene as the major phase and polystyrene or polyethylene terephthalate as the minor phase and optional compatibilizers; they were employed as starting membrane materials at concentrations not exceeding 15% by wt. The blends were first compounded in a corotating twin-screw extruder and subsequently extruded through a sheet die to obtain the non-porous precursor films (5, 6). These were uniaxially or biaxially drawn (100-500%) with respect to the original dimensions at a temperature below the glass transition temperature of the minor phase to induce a microporous structure and then post-treated at elevated temperatures to stabilize the porous structure, which consisted of uniform microcracks in the order of a few nanometers in width. Different mixing protocols were also employed to control the

morphology of the membranes. The original thickness of the precursor film was 50-100 micrometers and after stretching its thickness ranged from 10 to 30 micrometers.

## Results

The microporous films were produced from the immiscible PP blends through melt processing followed by post-extrusion treatments to induce porosity and generate microcracks at the domain interface of the immiscible blend. In the dispersed blends, phase domains of the minor component were expected to act as stress concentrators and enhance the local stress within the blend microstructure for the formation of microcracks upon stretching. The effects of blend composition and extrusion process parameters on surface and cross-sectional porosity and solvent permeability of the prepared films were related to specific microstructural features of the films before and after drawing. Finite element modeling of the stretching operation in the solid state yielded a successful interpretation of the blend response to uniaxial tension that resulted in microcrack formation (7). Rates of microcrack initiation and growth depend strongly upon applied stress condition and deformation temperature. The stretched films contained three-dimensional uniform microcracks in the order of a few hundred Angstroms in width across the thickness of the membranes. Micrograph reveal that the porous structure on the surface is connected to the interpenetrating network of microcracks throughout the thickness of the membrane. The microporous polymeric membranes obtained from this process have transport and mechanical properties that are suitable for membrane processes that operate at 2 to 10 bars at room temperature. (Fig. 1).

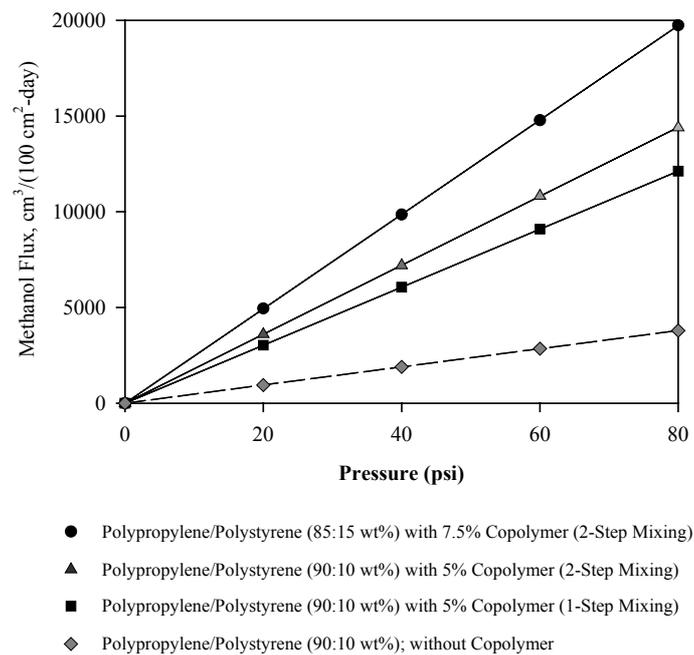
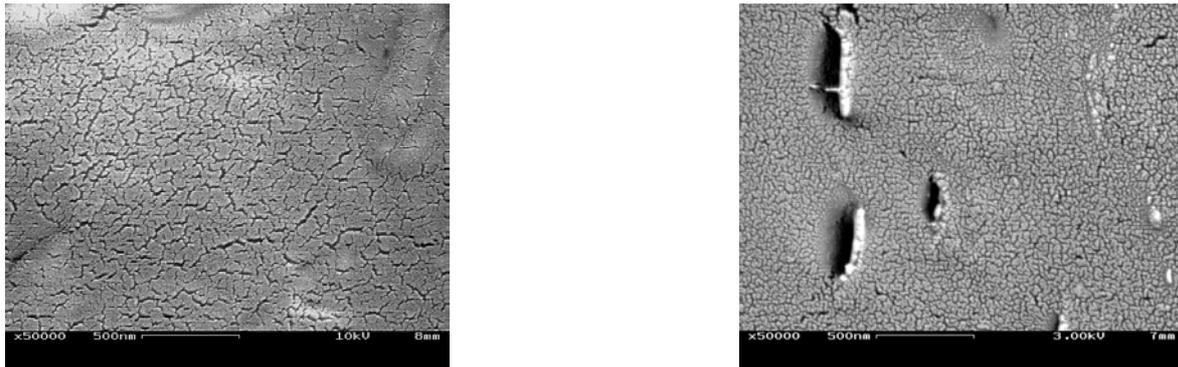


Fig. 1. Plots showing flux of methanol through different membranes as a function of pressure

A block copolymer (SEEPS) composed of hard and soft blocks was used as the interface modifier in the PP/PS blends to strengthen the interface in a material that was subsequently deformed. The block copolymer promoted more efficient stress transfer across the interface and enhanced the stress concentration in the matrix. The pattern of stress distribution changes in the film lead to different modes of microcrack formation, depending on both the concentration and mode of addition of the copolymer during melt mixing. The size, size distribution and shape of the dispersed phase as well as

the degree of interfacial adhesion which are important factors to determine the structure of the membrane were controlled by adjusting processing conditions as well as concentrations of the dispersed phase and copolymer. The addition of the block copolymer had remarkable effects on the membrane structure such as changes in the density and uniformity of the microcracks in comparison to the binary PP/PS blends. Cross-sectional views of the two membranes with and without compatibilizer are compared in the accompanying microphotographs (Fig. 2). It is shown that the block copolymer promotes the formation of a finer morphology characterized by an interpenetrating network of microcracks along the thickness of the membrane. This type of morphology is required for mass transport across the microporous film and results in enhanced permeability to solvents.



**Fig. 2** a) Electron Micrograph illustrating a cross section of a microporous membrane based on PP/PS blend without copolymer. 50,000x (left)  
b) Electron Micrograph illustrating a cross section of a microporous membrane based on PP/PS/copolymer blend. 50,000x (right)

The processes developed in this work may be considered as solventless alternatives to phase inversion-manufacturing practices for membranes containing mesopores. Comparison of some of the novel microporous structures with commercial membranes prepared by solvent-based phase inversion processes suggests comparable pore size and porosity ranges, with narrower pore size distribution (Table 1).

Membrane	Pore Diameter (nm)			Surface Porosity (%)
	Min.	Max.	Mean	
Amicon PM30	1.5	9.8	4.0	5.9
Amicon XM100A	2.1	13.5	6.1	4.4
Amicon XM300	2.1	22.3	8.6	6.4
Millipore PTTK	2.5	6.4	4.8	5.5
Millipore PTHK	1.5	45.9	9.2	9.9
PP/PS (90/10)	4.4	15.7	10.1	11.1
PP/PS/SEEPS (90/10/5); 1-Step Mixing	3.1	10.1	5.3	13.2
PP/PS/SEEPS (90/10/5); 2-Step Mixing	3.7	13.1	6.2	10.8
PP/PS/SEEPS (85/15/7.5); 1-Step Mixing	4.1	22.2	9.2	12.1

*Table 1. Comparison of surface pore characteristics of experimental membranes based on PP/PS blends with commercial membranes (data for commercial membranes from Ref. 8)*

## Summary

Novel microporous membranes with pore size ranging from 2 to 25 nm were produced from immiscible polypropylene blends via melt processing and post-extrusion treatments. The melt processing method employed in this research has several potential advantages over other membrane fabrication processes, especially for solvent-resistant membranes: low environmental impact; membrane structure can be tailored by adjusting blend components and/or process parameters; high production rates resulting in lower production cost; a wide variety of polymer systems having different physical and chemical properties can be used as starting materials.

## References

1. M. L. Druin, J. T. Loft, and S. G. Plován, *Novel open-celled microporous film*, US Patent 3,801,404, 1974.
2. H. S. Bierenbaum, R. B. Isaacson, M. D. Druin, and S.G. Plován, *Microporous polymeric films*, I&EC Prod. Res. Develop., 13, 2 (1974)
3. H. S. Bierenbaum, L. R. Daley, D. Zimmerman, and I. L. Hay, *Process for preparing a thermoplastic microporous film involving a cold stretching step and multiple hot stretching steps*, US Patent 3,843,761, 1974.
4. Brazinsky, W. M. Cooper, and A. S. Gould, *Process for preparing a microporous polymer film*, US Patent 4,138,459, 1979.
5. C. Chandavasú, M. Xanthos, C. G. Gogos, and K. K. Sirkar, *Preparation of microporous film from immiscible blends via melt processing*, J. Plast. Film Sheet, 16, 288 (2000) .
6. C. Chandavasú, Ph.D. Dissertation, New Jersey Institute of Technology, Newark, NJ, 2001
7. C. Chandavasú, M. Xanthos, K.K. Sirkar and C.G. Gogos, *Polypropylene Blends as Materials for Microporous Membranes Formed by Melt Processing*, Polymer, 43, 781 (2002)
8. K. J. Kim, A. G. Fane, C. J. D. Fell, T. Suzuki, and M. R. Dickson, *Quantitative microscopic study of surface characteristics of ultrafiltration membranes*, J. Membrane Sci., 54, 89 (1990).