

FORMATION AND MICROSTRUCTURE OF POLYETHYLENE MICROPOROUS MEMBRANES THROUGH THERMALLY INDUCED PHASE SEPARATION

LI Wenjun(李文俊)

(Department of Macromolecular Science, Fudan University, Shanghai 200433, China)

YUAN Youxin(袁又欣) and CABASSO, Israel

(The Polymer Research Institute, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210, U. S. A.)

ABSTRACT

Microporous membranes of low-high density polyethylene and their blends were prepared by thermally-induced phase separation of polymer/long-aliphatic chain alcohol (diluent) mixtures. The microstructures of this particular membrane, which depends on the diluent properties, polymer concentration and cooling rate, were observed by scanning electron microscopy. "Beehive-type," leafy-like, and lacy porous structure morphologies can be formed, depending on the blend composition and phase separation conditions, which were discussed by the polymer and diluent crystallization processes.

INTRODUCTION

Functionalized microfiltration membranes are currently used in a variety of fields, such as ion-exchange, electrochemical cell, facilitated transport^[1], environment - sensitive materials^[2], etc. Microporous membrane functionalizations are usually performed by chemical reaction modifications onto the matrix surface of microporous membranes. The matrix material of functionalized microporous membranes is required to have good thermal and solvent resistance, considerable physical strength and be inexpensive. Based on our previous studies^[3], low density polyethylene (LDPE) is one of the ideal materials. LDPE is a commercial semicrystalline polymer, in which the amorphous regions can be modified by chemical reactions, while the crystalline regions act as a "crosslinking side" to fix the membrane shape. However, the traditional processes of microporous

membrane formation, such as sintering of crystalline polymer powders, stretching of extruded high crystalline polyolefin films, track etching of polymer films, and phase inversion solution casting of polymers, have their limitations for LDPE use. A new preparation technique of microporous membranes via thermally induced phase separation (TIPS) has been developed since 1980^[4]. Since then, a variety of polymer diluent systems have been studied^[5-10] in order to demonstrate the applicability of this method for microporous membrane formation and, so far, the LDPE-diluent system has not yet been reported. In addition, quite a few potential applications, such as microfiltration, ultrafiltration, cloth laminates (permeability to water vapor, but not liquid water), membrane distillation, controlled release materials, catalytic substrates, and multishell fusion targets for laser interaction experiments^[5] etc. are being developed for this kind of microporous material.

Generally, the TIPS process consists of the following steps:

1. A homogeneous solution is formed at an elevated temperature by blending the polymer with a high-boiling point, low molecular weight liquid or solid diluent;
2. The solution is then cast into the desired shape (flat sheet, tube or hollow fiber);
3. The solution is cooled at a controlled rate or quenched to induce phase separation;
4. The diluent is removed (typically by solvent extraction) to produce a microporous structure.

As a section of functionalized microporous membrane series, this paper presents the formation of PE microporous material via the TIPS method and discusses the relationships between the structure of the microporous material and diluent properties, polymer concentration, and cooling rate.

EXPERIMENTAL

Materials

LDPE pellet (Tenite 1810E, MI: 1.0g/10 min), purchased from the Eastman Kodak Company, and HDPE pellets (Paxon) from Allied Chemical Fiber and Plastics Company. The properties and sources of the diluents are shown in Table 1. The materials were used as received without further treatments.

Table 1 Properties of diluents used

Name	Formula	M. W.	B. P. (°C)	M. P. (°C)	Density (g/ml)	Source
1-Dodecanol	C ₁₂ H ₂₅ OH(98%)	186.34	260—262	24—27	0.82	Aldrich Chem.
1-Hexadecanol	C ₁₆ H ₃₃ OH(99%)	242.45	180/10mm	54—56		"
1-Octadecanol	C ₁₈ H ₃₇ OH(99%)	270.50	170—171/2mm	60—61		"
Octadecane	C ₁₈ H ₃₈ (99%)	254.50	317	28—30	0.78	"
Mineral Oil						Fisher Scientific

Preparation method

Homogeneous polymer-diluent solutions were prepared as follows: LDPE pellets (ca. 2g) and appropriate amounts of diluent were weighed into a 24 ml vial. The vial was purged with nitrogen, sealed with aluminum foil and heated to 170—180°C in an oil bath for 10 minutes to ensure the melting of the crystalline polymer. The melt polymer-diluent combination was completely blended with a glass stir to form a homogeneous solution. The solution was set in an oil bath for 5 minutes to remove air bubbles, then the vial was slanted and turned around so that the solution would be cast on the wall of the vial. The vial was removed from the oil bath (180°C) and cooled at room temperature in ice water or cooled at a controlled rate to solidify the blend. The solidified sample was removed from the vial and immersed in acetone (or in other extractants) overnight to extract the diluent. The diluent-free sample was heated in a vacuum oven at 40°C for two hours to vaporize the extractant. Finally, the white microporous material was obtained.

SEM observation

The microstructure of microporous membranes were examined using an ETEC Corporation Autoscan scanning electron microscope (SEM). The cross-section of the sample for SEM observation was obtained by immersing the sample in liquid nitrogen and breaking it. The broken sample was adhered on the sample stage using colloidal graphite, and placed in a sputtering coater for vacuum metallizing with gold, then viewed using SEM.

Determination of crystallization temperature

The dependence of crystallization temperature of the PE-C₁₂ OH blends on the compositions and the effect of cooling rate on the crystallization temperature were determined using a Perkin-Elmer DSC-4 differential

scanning calorimeter (DSC) calibrated with indium. The blend samples of the PE-diluent prepared by the method outlined above were weighed and sealed into an aluminum pan. The pan was heated to 145°C in the DSC to ensure the samples complete melting, then cooled at a desired cooling rate. The crystallization temperature was taken as the peak temperature on the exotherm.

RESULTS AND DISCUSSION

Diluent effects

Mobility (diffusion), crystallization of the diluent in polymer and its interaction with polymer significantly affect the structure of microporous membranes formed by the TIPS process. Several long, aliphatic-chain alcohols, whose properties are shown in Table 1, were selected as diluents in this study because they have a certain polarity, low toxin, and are inexpensive. Figs. 1 and 2 show SEM photomicrographs of the membranes prepared by different diluent-LDPE systems in the same composition and cooling condition. As shown in Figs. 1 and 2, there are considerable differences in the structure and morphology of the membrane cross-section. For the LDPE-C₁₂OH sample, Fig. 1, a "beehive-type" structure of large inter-spherulitic voids and smaller intra-spherulitic voids were obtained. Formation of the structure was attributed to the solid-liquid phase separation of the homogeneous LDPE-C₁₂OH blend during cooling. When the melted LDPE-C₁₂OH solution was cooled and the temperature was above the melting point of C₁₂OH, the LDPE crystallized and the spherulites were formed. As the spherulites grow, some of the diluent is rejected from the LDPE spherulites into the LDPE amorphous regions. After the diluent is extracted, the voids between the spherulites (inter-spherulitic regions) were formed. Also, some of the diluent was entrapped between lamellae within the spherulites, which will produce the intra-spherulitic voids (inter-lamellar regions).

For LDPE-C₁₆OH, LDPE-C₁₈OH and LDPE-C₁₈H₃₈ systems, the length of the aliphatic chain of diluents increases, the melting point increases, and the molecular polarity decreases. The structure of the membrane cross section is considerably different than the LDPE-C₁₂OH sample. From Fig. 2, we found that the surface of LDPE spherulites was covered with a layer of hair-like LDPE crystalline. It is difficult to find if there are voids within spherulites. This result probably relates to the competition growth of

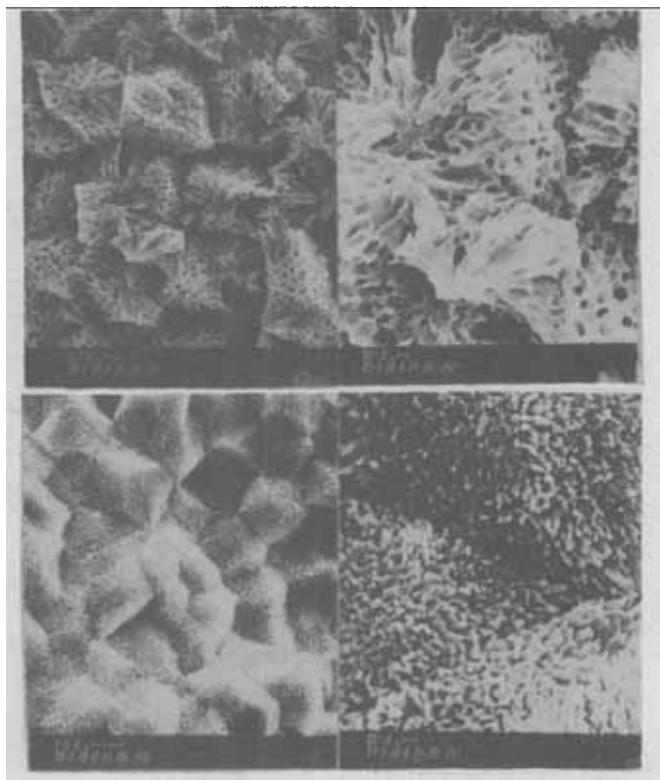


Fig. 1 Diluent effect on LDPE membrane structure (40 wt% LDPE, quenched from 180°C to room temperature, 23°C.
Top: LDPE-dodecanol; Bottom: LDPE-1-hexadodecanol;
Left: low magnification; Right: high magnification)

crystallization of LDPE and diluents. Table 1 indicates the melting points of $C_{16}OH$, $C_{18}OH$, and $C_{18}H_{38}$ are close to 55, 61 and 29°C, respectively. When the cooled temperature was below the equilibrium crystallization temperature of the diluents, both LDPE and the diluent would crystallize, but LDPE crystallizes prior to that of the diluent, due to a larger degree of supercooling of LDPE. Consequently, the diluent rejected from LDPE spherulites has to crystallize on the surface of formed LDPE spherulites. Because the growth rate of the diluent crystallization is faster (molecular weight low) than that of LDPE, the growth of LDPE crystallization (some of the LDPE comes from the polymer-lean phase) will be limited to between the gaps of the diluent crystalline to form the hair-like crystalline structure.

For the LDPE-mineral oil samples, chloroform was used as the extractant due to less miscibility of acetone with mineral oil. No discernible phase separation structure was observed. Actually, mineral oil is a mixture of n-alkane with a different chain length (a homologue of LDPE). Better

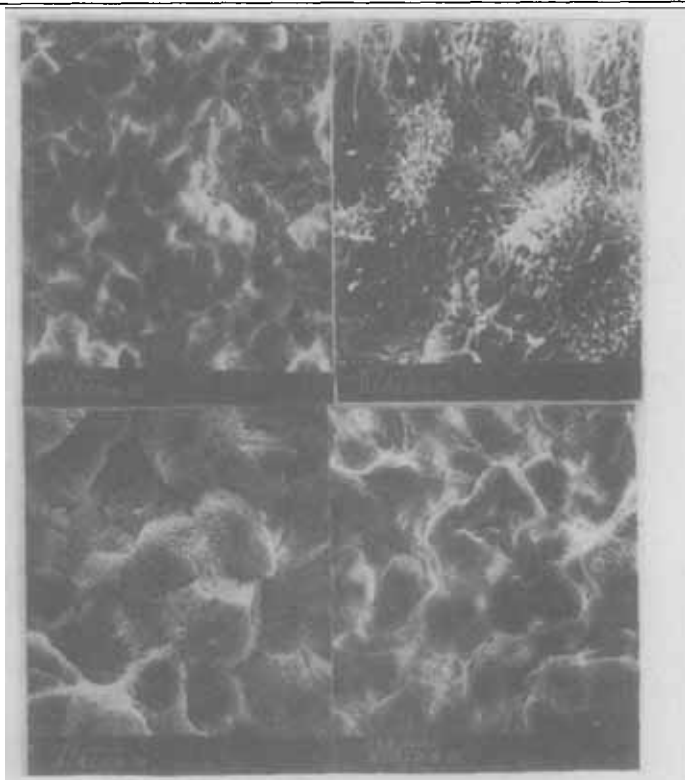


Fig. 2 Diluent effect on LDPE membrane structure (40 wt% LDPE, quenched from 180°C to room temperature, 23°C.
Top: LDPE-1-octadecanol; Bottom Left: LDPE-C₁₈H₃₈;
Bottom Right: LDPE-mineral oil)

miscibility with LDPE at room temperature results in lack of the microporous structure formed from phase separation. However, further experimentation is required for this system.

Composition effects

In the previous section, the effects of the diluent were examined at a fixed composition of 40 wt% LDPE and a fixed cooling condition. However, the effects of the composition on the membrane structure are also important since the phase separation may be altered by the initial composition and the degree of supercooling. The effects of composition on the TIPS membrane structure were observed for the LDPE-C₁₂ OH and HDPE-C₁₂ OH systems. Compositions of 30, 40, 50, and 60 wt% LDPE and 10, 20, 30, 40 and 50 wt% HDPE were selected in this study at a fixed cooling temperature (from 180°C to room temperature, 23°C). As shown in Figs. 3 and 4, the pore size of inter and intra-spherulites decreases, and the spherulitic population increases when the LDPE content increases. The increase of spherulitic population is

Fig. 3 Composition effect on the membrane structure of LDPE-dodecanol samples (quenched from 180°C to 23°C; Top: 30 wt% LDPE; Bottom: 40 wt% LDPE)

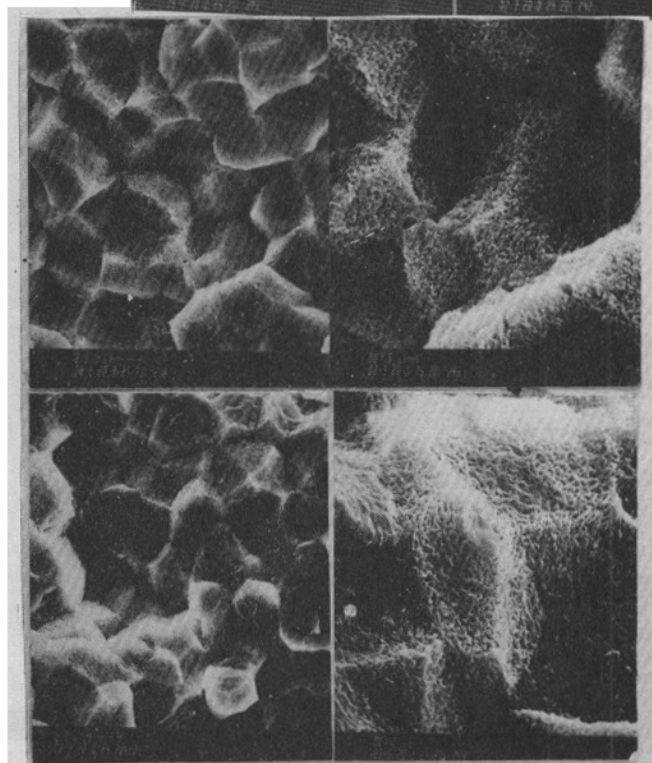
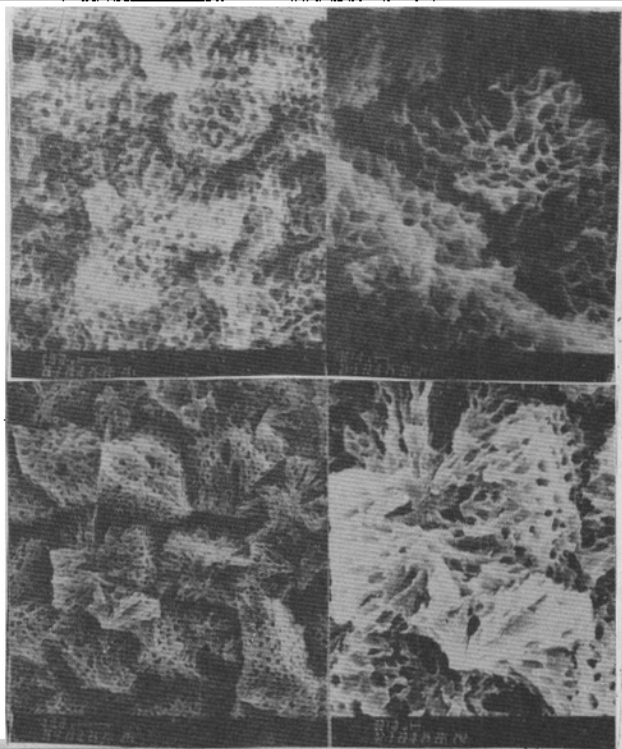


Fig. 4 Composition effect on the membrane structure of LDPE-dodecanol samples (quenched from 180°C to 23°C; Top: 50 wt% LDPE; Bottom: 60 wt% LDPE)

Fig. 5 Composition effect on the membrane structure of HDPE-dodecanol samples (quenched from 180°C to 23°C, Top: 20 wt% HDPE; Bottom: 30 wt% HDPE)

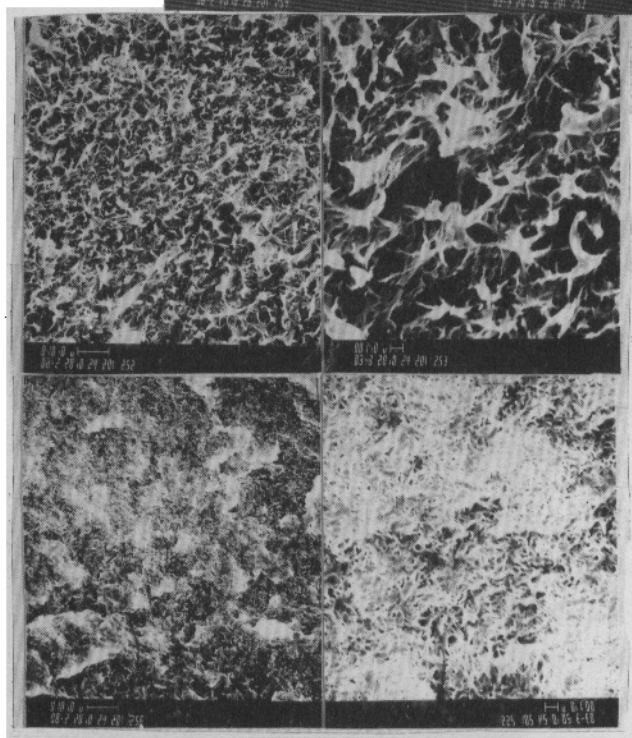
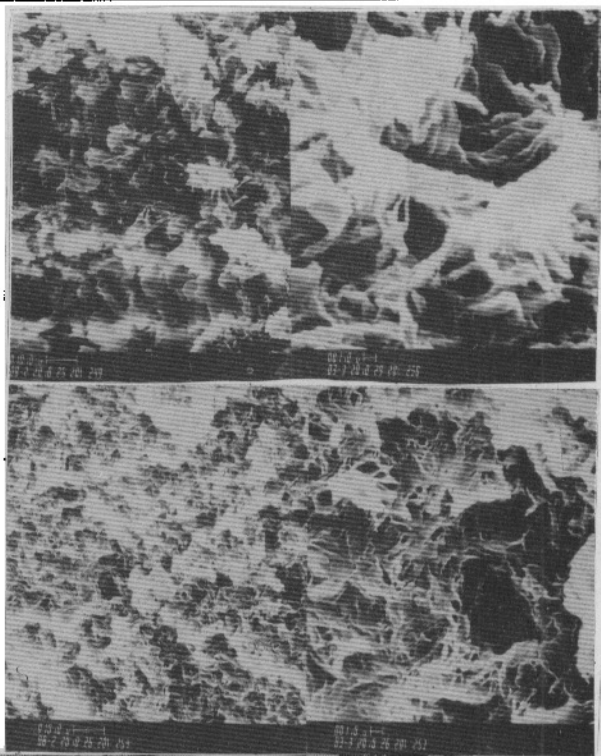


Fig. 6 Composition effect on the membrane structure of HDPE-dodecanol samples (quenched from 180°C to 23°C, Top: 40 wt% HDPE, Bottom: 50 wt% HDPE)

due to an increased nucleation density at the higher LDPE concentration. Thirty and 40 wt% LDPE samples were compared with that of 50 and 60 wt%. In addition to the decrease in pore size, the morphology of the spherulites were also changed. Because of the nucleation density increase for 50 and 60 wt% LDPE samples, the spherulites infringed on each other and the growth of spherulites was limited, which resulted in a spherulitic shape with sharp edges. Dependencies of composition on the TIPS membrane structure for HDPE- $C_{12}OH$ samples were shown in Figs. 5 and 6. There is a significant difference between the structure of the membrane cross-section and the LDPE- $C_{12}OH$ samples. No discernible spherulites were exhibited in the range of 10–60 wt% HDPE, and a leafy structure was formed. The packing density of the HDPE microporous materials increases with the increase of the concentration of HDPE in the blend. At the composition above 60 wt% HDPE, the samples will not exhibit microporous structure. Also, when the HDPE content was below 20 wt% in the HDPE- $C_{12}OH$ blend, the samples produced by the TIPS process have no structural integrity. For the HDPE-mineral oil system, a similar leafy structure has been observed^[10]. It has been reported^[11] that the lamellar-like crystallites can be formed for the linear PE with high molecular weight fraction in melt crystallization. Thus, these randomly-oriented, curved, polymer leaves in the samples are believed to be stacked lamellae. However, we still do not know why the spherulites were formed for the LDPE and why the lamellae structures were obtained for HDPE in the same TIPS process.

Effects of the cooling rate

Due to the fact that the membrane preparation via the TIPS process is a nonequilibrium process, the crystallization curves for the LDPE- $C_{12}OH$ system at three cooling rates (-15 , -25 and $-35^\circ C/min$) were determined by DSC (Fig. 7). The results indicate that the crystallization temperatures at which the solid-liquid phase separation occurred depress with the increase in the cooling rate because of the supercooling phenomenon. It demonstrates that the effects of the cooling rate on membrane formation should be considerable. With the higher melt viscosity and longer relaxation time, the crystallization temperature of the LDPE was much lower than that of LDPE in blends, when cooling rates were $-25^\circ C$ and $-35^\circ C/min$ (See Fig. 7)

Fig. 8 shows the photomicrographs of samples formed with different cooling rates at a fixed composition (30 wt% LDPE- $C_{12}OH$) and at a post-treatment condition. There are no obvious structure differences between

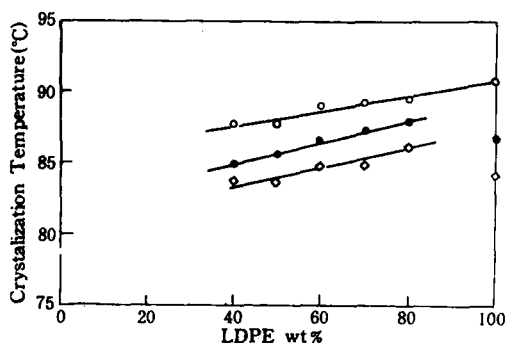


Fig. 7 Crystallization temperature vs. composition for LDPE-C₁₂ OH system.

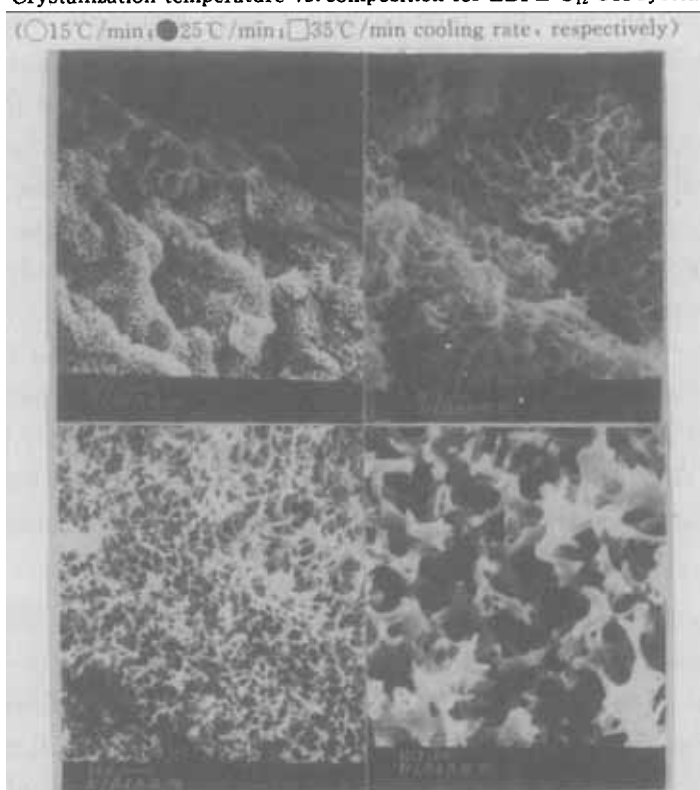


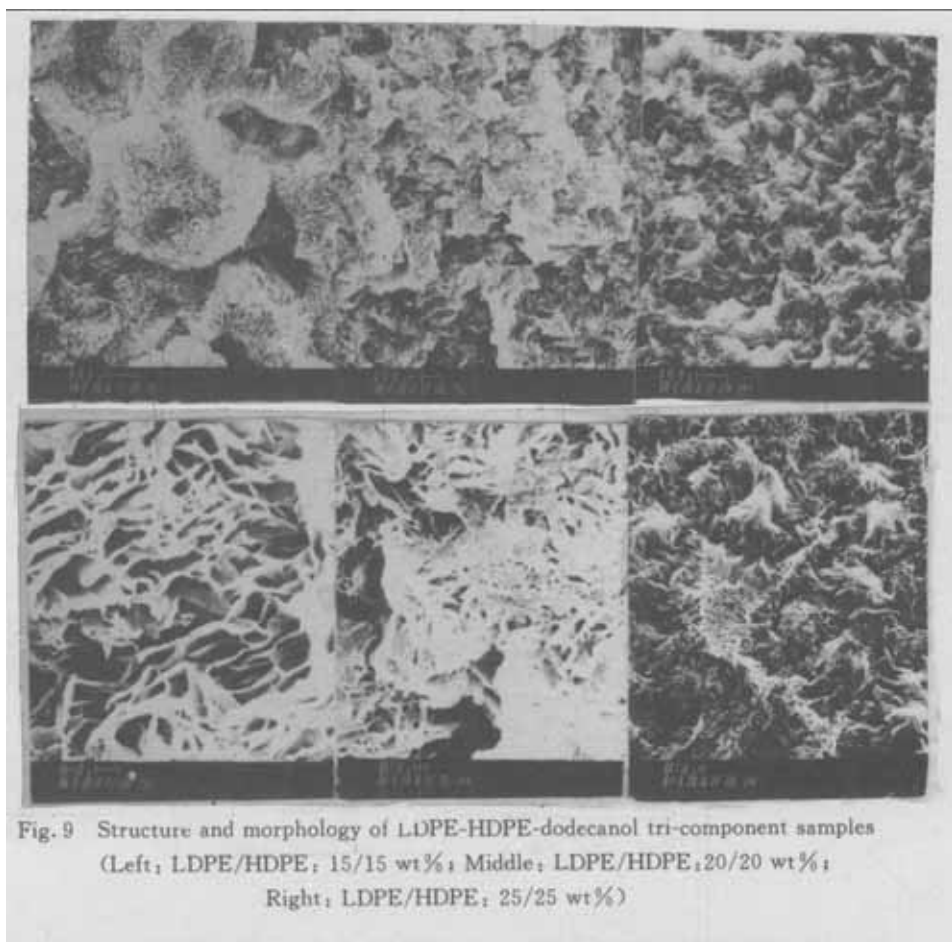
Fig. 8 Effect of the cooling rate on the membrane structure of LDPE-dodecanol (30 wt% LDPE) samples.

Top: quenched from 180 °C to room temperature;

Bottom: quenched from 180 °C into ice water

samples cooled at 15 °C/min and cooled from 180 °C to room temperature. However, the structure of the resulting sample cooled in ice water was quite different from the former samples. A lacy structure with very high porosity was formed. Lloyd et al.^[12] has reported a similar lacy structure obtained

from melt isotactic polypropylene (25 wt%)/N,N-bis (2-hydroxyethyl) tallowamine mixtures quenched from 533K to 318K in water, while the mixture cooled at 10K/min from 533K to 318K, the cellular structure was formed. Their discussion was in terms of the thermodynamics of the binary mixture and possible phase separation mechanisms, and they suspected that the formation of the lacy structure was attributed to liquid-liquid phase separation. Based on this mechanism, once the liquid-liquid phase separated, the diluent-rich domains were entrapped within the LDPE spherulites and, thus, retained their original shape and size. The growth of LDPE spherulites was restricted in a small space, preventing the development of LDPE spherulites and yielding a lacy structure. In order to confirm this explanation, further experimentation is required.



Structure of LDPE-HDPE-diluent tricomponent blend

The samples comprised of the same amounts of LDPE and HDPE with different ratios of diluent (dodecanol) were prepared. The cross-section structures of the resulting samples are shown in Fig. 9. The photomicrographs of the samples indicate that the membrane structures formed from tricomponent blends via TIPS are more complicated. It seems that a medium structure lying between the LDPE spherulitic and the HDPE leafy structures were presented. When the polymer (LDPE & HDPE) concentration was 30 wt% (Fig. 9), a leafy-type lamellar crystalline was produced on the surface of large spherulites. With the polymer concentration increasing, the spherulites and porosity in the membrane were depressed. When the polymer concentration was above 40 wt%, the membrane structure became more concentrated, but the inter-spherulitic voids and the surface voids of spherulites can still be distinguished.

Fig. 10 shows the crystalline melting temperature characterized by DSC for LDPE, HDPE and its blend membranes formed via the TIPS process. It can be seen that the crystalline melting temperature of blend membranes lies between that of LDPE and HDPE. This result represented the miscibility of the LDPE and HDPE, not only for amorphous regions, but also in the crystalline regions (the remaining LDPE peak in the blend samples disappeared after the second scanning). The syngenetic crystalline of the LDPE and HDPE resulted in a special structure morphology of the membranes.

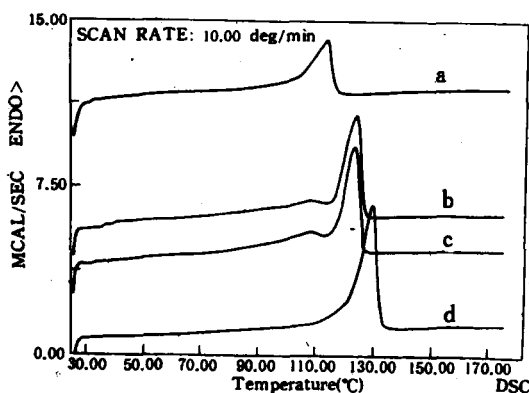


Fig. 10 Melting behavior of LDPE(a), HDPE(d) and their blend(b,c) microporous membranes formed by TIPS process

Keywords:

Microporous membrane; Membrane preparation; Membrane structure; Phase separation; Polyethylene membrane

REFERENCES

- [1] leBlanc, O. H. ; Ward, W. J. ; Matson, S. L. , et al. , *J. Membrane Sci.* , **1980**, 6, 339.
- [2] Iwata, H. and Matsuda, T. , *J. Membrane Sci.* , **1988**, 38, 185.
- [3] Cabasso, I. ; Korngold, E. and Liu, Z. Z. , *J. Polymer Sci. , Polym. Letters Ed.* , **1985**, 23, 577.
- [4] a) Castro, A. J. , *U. S. P.* 4, 247, 498, Jan. 27, **1980**.
b) Shipman, G. H. , *U. S. P.* 4, 539, 256, Sept. 3, **1985**.
- [5] Caneba, G. T. and Soong, D. S. , *Macromolecules*, **1985**, 18, 2538.
- [6] Aubert, J. H. and Clough, R. L. , *Polymer*, **1985**, 26, 2047.
- [7] Williams, J. M. and Moore, J. E. , *Polymer*, **1987**, 28, 1950.
- [8] Hikment, R. M. ; Callister, S. and Keller, A. , *Polymer*, **1988**, 29, 1378.
- [9] Williams, J. M. and Moore, J. E. , *Polymer*, **1989**, 30, 2279.
- [10] Lloyd, D. R. ; Kinzer, K. E. and Tseng, H. S. , *J. Membrane Sci.* , **1990**, 52, 239.
- [11] Voight-Martin, I. G. ; Fisher, F. W. and Mendelkern, L. , *J. Polym. Sci. , Polym. Phys. Ed.* , **1980**, 18, 2347.
- [12] Lloyd, D. R. ; Kim, S. S. and Kinzer, K. E. , *J. Membrane Sci.* , **1991**, 64, 1.