Microporous Polypropylene Films Containing Ultrafine Silica Particles

YUKIO MIZUTANI, SATOSHI NAGŌ

Tokuyama Corporation, Tokuyama-City, 745-0053 Japan

ABSTRACT: Sol–gel reaction of tetraethoxysilane was carried out in molten polypropylene with the aid of an extruder. The resultant composites were used to mold sheets containing finely dispersed SiO_2 particles. These sheets were biaxially stretched to prepare microporous films, of which some properties were estimated (pore size, porosity, specific surface area, and gas permeability). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1489–1494, 1999

Key words: polypropylene; microporous film; tetraethoxysilane; sol–gel reaction; extruder

INTRODUCTION

Various microporous materials (membranes, sheets, and hollow fibers) are used practically in various ways.[1–5] We reported that microporous polypropylene (PP) sheets are prepared by biaxially stretching PP sheets containing fillers such as $CaCO_3$, SiO_2, and polymethylsilsesquioxane.[6–8] The microporous structure is controllable by adjusting the filler content, the particle size of the filler, and the stretching ratio. The microporous PP sheets have fibrous PP texture in which the filler particles are dispersed. To make the fibrous texture relatively finer, the use of the filler with relatively smaller particle size is preferable. However, there is an inevitable limit regarding the pore size, that is, the fineness of the fibrous PP texture. Namely, fine particles generally have a natural tendency in which the smaller the particle size, the more the particles tend to aggregate. Accordingly, uniform dispersion of the filler particles in any substrate becomes difficult with decreasing the particle size and the aggre-

gated particle size becomes effective regarding the formation of the microporous structure.

On the other hand, some investigators reported sol–gel reaction of tetraethoxysilane (TES) in some polymers, such as poly(dimethylsiloxane), polyamide, and polyvinyl acetate, and showed that the size of the resultant SiO_2 particles are of the order of 0.01 μm, dispersed uniformly in the substrate polymer phases.[9–12]

We succeeded in sol–gel reaction of TES in molten PP with the aid of an extruder. The resultant SiO_2 particles were minute and uniformly dispersed in the PP phase. The base sheets were molded from the resultant PP composite and, subsequently, biaxially stretched to prepare microporous PP films. We report the preparation of the microporous PP films and their properties.

EXPERIMENTAL

Materials

The PP powder used was PN-120 from Tokuyama Corp. [melt flow index (MFI), 1.2 g/10 min at 230°C]. All reagents used were of chemical grade and 2,6-di-*t*-butyl-4-methylphenol was used as an antioxidant.

Profile

Figure 1 Sketch of the extruder.

Preparation

The extruder used was equipped with twine screws 2-D25-S from Toyo Seiki Co., Ltd. (Fig. 1)

and the plunger pump used was HYM-03-P from Fuji Tekuno Kogyo Co., Ltd. to feed TES or H_2O into the extruder. The preparative procedure is shown below.

PP powder, the antioxidant, and a definite amount of Ca–stearate (Ca–St) were mixed well in advance and extruded to prepare pellet A with constant feeding of TES (about 65 mL/

min). The resultant pellet A was extruded again with constant feeding of H_2O (1.3 mL/min) to hydrolyze TES; pellet B was equally prepared. After drying, the resultant pellet B was ex-

Figure 2 Effect of the screw rotating speed to MFI and ash content. Ca–St content (1.5%) and the screw rotating speed were same in the cases of feeding TES and water.

truded to mold the base sheet, which was biaxially stretched to prepare microporous PP film by using a biaxially stretching machine of pantagraph type, Type I (Brückner Co.).

Measurement

Determination of SiO$_2$ Content

A piece of microporous PP sheet (5 g) was put into a porcelain crucible and heated for 2 h to incinerate organic components. The residual ash was weighed.

Porosity, Pore Size, and Specific Surface Area

Porosity, pore size, and specific surface area were measured by using an Hg porosimeter, Poresizer 9310 (Shimadzu Corp.).

N$_2$ Gas Permeability

The sample was set between flanges sealed with rubber packings, as shown elsewhere.[8] The effective diameter of the sample was 20 mm. N$_2$ gas was supplied into the chamber through a pressure regulator. N$_2$ gas flux was measured at room temperature by a digital flow meter, Model 2500SS (Sōgō Rikagaku Industry Co.).

Scanning Electron Microscopy

The scanning electron microscopes used were JSM-220 and JSM-6400F (JEOL Ltd.). Pretreatment of each sample was carried out by using Au–ion sputtering for 3 min at 1.2 kV and 8–10 mA.

RESULTS AND DISCUSSION

Sol–Gel Reaction

It was found that TES is compatible with molten PP and contained in PP phase even after cooling. On the other hand, it is well known that Ca–St is compatible with PP. Then, PP, TES, and Ca–St make a homogeneous phase in the molten state by kneading it with the aid of the extruder. By plunging water into the extruder, water vapor reacts with TES and Ca–St, both of which are hydrolyzed. The resultant pellets are in a state of foam, owing to evolved ethanol and water vapors. The resultant Si—OH groups form Si—O—Si bonds, promoted by Ca^{2+} and high temperatures. Because the molten PP as the reaction medium is

Figure 3 Effect of Ca–St content to MFI and ash content. Both the screw rotating speeds in the cases to feed TES and water were 30 rpm.

Table I   Effect of the Ash Content to Structure of Microporous PP Films

Sample No.	Ash Content (%)	Stretching Ratio	Porosity (%)	Pore Size (μm)	Specific Surface Area (m^2/g)	K (cm^2/s)
1	2.2	3.5	8.4	0.01	114	0.010
2	2.6	5	13.3	0.02	161	0.016
3	2.8	3	15.0	0.02	177	0.052
4	3.4	4	19.1	0.02	189	0.083

Stretching ratios were the same both in the machine and in the transverse directions at 150°C. Film thickness, 6–9 μm.

highly viscous, the diffusion rate of TES to the reaction points should be so small that the resultant SiO$_2$ particles are minute and uniformly dispersed in the PP substrate.

Also, some amount of TES was inevitably lost at the blending process of TES with PP in main. Therefore, the reaction yield was estimated by determining the ash content of pellet B. The pellets after the hydrolysis were again extruded to exclude the foam described before to make the molding of the base sheet easily possible.

Figure 2 shows the results of the sol–gel reaction in relation to the screw rotating speed, when the Ca–St content was constant. When the screw rotating speed is relatively large, the TES amount fed into the molten PP becomes relatively small. Accordingly, the ash content reasonably becomes smaller with increasing the screw rotating speed, and the MFI is rather unchanged. Figure 3 shows the effect of the Ca–St content to the sol–gel reaction. When the screw rotating speed is constant (30 rpm), the increase of the Ca–St content causes the ash content and MFI to increase, which indicates the effectiveness of Ca–St as the catalyst to the sol–gel reaction. Also, it is interesting to note that MFI increases with increasing ash content, probably because of the increase of unreacted Ca–St and the resultant stearic acid, which have a lubricating effect.

Here, the ash content is used as a measure of SiO$_2$ content because the amount of Ca incorporated into the SiO$_2$ component is obscure. Also, the residual Ca–St transforms to CaCO$_3$ by the incineration. Then, the CaCO$_3$ content was estimated assuming that all Ca–St added transformed into CaCO$_3$; the CaCO$_3$ contents are small, 0.16–0.4%, corresponding to the Ca–St contents, 1–2.5% (Fig. 3). Therefore, the participation of Ca–St was neglected.

Structure of Microporous PP Films

When the base sheet is stretched in the machine direction, the PP phase is split at the periphery of very small SiO$_2$ particles and the resultant micropores are widened by subsequent stretching in the transverse direction, as reported elsewhere.[7] Here, the key point is the fact that very minute particles are uniformly dispersed in the PP phase with no aggregation. This is a breakthrough relating to the ordinary tendency that the smaller the particle size, the more the particles tend to aggregate.

Table I shows the effect of the ash content to the structure of the microporous PP films. When the stretching ratios are 3.0–5.0 both in the machine and transverse directions, the increase of the ash content makes the microporous structure finer. The pores are minute and the specific surface area and porosity become larger with increasing ash content.

N$_2$ Gas Permeability

N$_2$ gas permeability was estimated by using some microporous PP films with the various ash contents. Figure 4 shows relationships between N$_2$ gas flux and pressure difference across the films, prepared under the conditions shown in Table I. The linear relations are observed and the permeability coefficients are estimated by using the following equation:

$$J = QA^{-l} = K\Delta Pl^{-l} \tag{1}$$

where J is the gas flux (cm^3 cm^{-2} s), Q is the volume permeation rate of the gas (cm^3/s), A is the effective area of the sample (cm^2), K is the permeability coefficient (cm^2/s), ΔP is the pressure difference across the sample (kg/cm^2), and l is the sample thickness (cm). The linear lines do

Figure 4 Dependency of gas flux (J) on pressure difference (ΔP).

Figure 6 An SEM of microporous PP film by using JSM-220.

not intersect the ordinate, so the pore size and tortuosity factor of pores could not be estimated according to the method by Yasuda and Tsai[13] and Cabasso et al.[14] Also, the linear lines intersect the abscissa. It means that there are limits of ΔP under which gas cannot permeate through the films, and the limit value increases with decreasing ash content, which supports the fact that the pore size is very minute as shown in Table I. Figure 5 shows the dependency of the permeability coefficient on the ash content as a measure of the SiO_2 content. The permeability coefficient sig-

nificantly depends on the ash content, although the stretching ratio varies in the range of 3–5. In general, gas permeability depends on pore size, pore number, and tortuosity factor of pores but not on porosity, and these factors are affected by the ash content, or in other words, the number of the SiO_2 fine particles. That is the reason the ash content was used here.

Scanning Electron Microscopy

Figure 6 shows a scanning electron micrograph of a microporous PP film, showing the distribution of the resultant SiO_2 particles. Here, the visual field was first closed tight under a magnification of 35,000, and then the depth of the focus was delicately adjusted. When the focus was slightly deep from the surface, white spots were observed. They resulted from the reflection of the electron beam by SiO_2 particles of which the electron density is larger than that of the PP substrate. Also, the black part shows the PP substrate damaged by electron beam. Accordingly, this pattern means that the SiO_2 particles are minute and uniformly dispersed in the PP substrate with no aggregation.

Figure 7 shows a scanning electron micrograph of the surface of microporous PP film. Many minute SiO_2 particles and pores are uniformly dispersed in a fibrous PP texture. Accordingly, the microporous PP films are transparent and these micrographs support the results described above.

Figure 5 Dependency of permeability coefficient (K) on ash content.

CONCLUSION

Sol–gel reaction of tetraethoxysilane was carried out in molten PP with the aid of an extruder. The

Figure 7 An SEM of the surface of microporous PP film by using JSM-6400F.

resultant polypropylene composites contain minute SiO_2 particles, which are uniformly dispersed in the PP substrate. This composite was molded to prepare the base sheets, which are subsequently biaxially stretched to prepare the microporous PP films. Their properties are as fol-

lows: pore size, 0.01–0.02 μm; porosity, 8–19%; and specific surface area, 80–189 m^2/g. Also, these films are transparent and gas permeable.

REFERENCES

1. Flinn, J. E., Ed., Membrane Science and Technology; Plenum: New York, 1970.
2. Kesting, R. E. Synthetic Polymer Membranes; McGraw–Hill, New York, 1971.
3. Hwang, S. T.; Kammermeyer, K. Membrane in Science, Wiley: New York, 1973.
4. Bierenbaum, H. S.; Isaacson, R. B.; Druin, M. L.; Flovan, S. G. Ind Eng Chem Prod Res Dev 1974, 13, 1.
5. Lonsdale, H. K. J Membr Sci 1982, 10, 81.
6. Mizutani, Y.; Kusumoto, K.; Nakamura, S.; Mizumoto, Y. Jpn Tokkyo Kōhō, Sho-53-21426, 1978.
7. Mizutani, Y.; Nakamura, S.; Kaneko, S.; Okamura, K. Ind Eng Chem Res 1993, 32, 221.
8. Nago, S.; Nakamura, S.; Mizutani, Y. J Appl Polym Sci 1993, 45, 1527.
9. Ning, Y. P.; Tang, M. Y.; Jiang, C. T.; Mark, J. E.; Roth, W. C. J Appl Polym Sci 1984, 29, 3209.
10. Sun, C. C.; Mark, J. E. J Polym Sci Polym Phys Ed 1987, 25, 1561.
11. Wang, S.; Ahmad, Z.; Mark, J. E. Polym Bull 1993, 31, 323.
12. Girard, E.; Reydet; Lam, T. M.; Pascault, J. P. Macromol Chem Phys 1994, 195, 149.
13. Yasuda, H.; Tsai, J. T. J Appl Polym Sci 1974, 18, 805.
14. Cabasso, I.; Robert, K. Q.; Klein, E.; Smith, J. K. J Appl Polym Sci 1997, 21, 1883.