NOTE

Microporous Polypropylene Films and Fibers Containing Finely Dispersed Vinyl Polymers with Crosslinkage

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INTRODUCTION

Recently, many investigators have been studying microporous films, membranes, sheets, and hollow fibers.¹⁻⁴ We also reported preparation of microporous polypropylene (PP) sheets.⁵⁻⁸ PP sheets containing fillers, such as SiO₂, CaCO₃, and poly(methyl silsesquioxane) are biaxially stretched to make them microporous. Their properties are controllable by adjusting the particle size and the content of the fillers and, also, the stretching degree. Here, the smaller the size of the filler particles, the smaller the resultant pore size, in general. However, when the size of the filler particles is of submicron size, the filler particles usually tend to aggregate more or less. Accordingly, uniform dispersion of the filler particles in any substrate is rather difficult, in general, and it makes the pore size distribution relatively broader.⁹ This means that there is an inevitable limitation to prepare the microporous PP sheets with relatively smaller pores because the aggregated particle size becomes effective.

On the other hand, PP composites are prepared by copolymerization of a vinyl monomer and divinyl benzene (DVB) in a molten PP phase with the aid of an extruder.¹⁰ Here, the vinyl monomer and DVB are compatible with the molten PP, but the vinyl polymer is not. Then, the propagating vinyl polymer radicals separate out of the molten PP phase, and DVB promotes this phase separation. Furthermore, diffusion of the vinyl monomer and DVB should be restricted in the very viscous, molten PP. Therefore, the resultant poly-(vinyl monomer-*co*-DVB) should become of minute particles, which are uniformly dispersed in the PP phase with no aggregation. Now, interaction of the vinyl monomer and/or DVB onto the PP molecule is obscure.

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In this article, we report the preparation of microporous PP films and fibers from the PP composites, using styrene (St) and glycidyl methacrylate (GMA) as the vinyl monomer and DVB as a crosslinking agent. Namely, the PP composites were prepared by copolymerization of St–DVB or GMA–DVB in molten PP phase with the aid of an extruder. Then, the base sheets were molded, which were biaxially stretched to prepare microporous PP films. Also, microporous PP fibers are prepared by melt-spinning and subsequent stretching. We estimated their properties.

EXPERIMENTAL

Materials

PP powder was PN-150 from Tokuyama Corp. (melt flow index at 230°C: 16 g/10 min). St, GMA, and DVB (55% purity) were of commercial grade and used with no purification. 1,1-Bis(*t*-butylperoxy) cyclohexane of commercial grade was used as an initiator of radical polymerization.

Preparative Procedures

Table I shows the recipes. St or GMA, and DVB and the initiator, are mixed well in advance. Then the monomer mixture was mixed with the PP powder, and they are extruded at $170-200^{\circ}$ C to copolymerize the monomers and prepare pellets with the aid of an extruder equipped with twin screws (rotating speed, 30 rpm). The resultant pellets were kept at 70° C overnight under a N₂ atmosphere and then again extruded with adding 2,6-di-*t*-butyl-4-methylphenol as an antioxidant, of which the content was 0.6% of PP powder. Subsequently, the pellets were extruded at 230°C to

| Sample | Monomer | DVB/(Monomer + DVB) | Initiator/(Monomer + DVB) | (Monomer + DVB)/PP | |
|--------|---------------------|---------------------|---------------------------|--------------------|--|
| А | St | 0.1 | 0.02 | 0.05 | |
| В | GMA | 0.08 | 0.02 | 0.05 | |

Table I Recipes^a

^a Weight ratio.

mold base sheets, which were biaxially stretched at 160–165°C by using a polymer film double spindle elongator, Model SS-60, from Shibata Scientific Co. Also, PP fibers were prepared by melt-spinning at 270°C and then stretched at 120°C to make the fibers microporous. Mechanical Properties. Tensile strength at yield (TS), Young's modulus (YM), and elongation at break were measured at 20 \pm 1°C with the aid of a tensile tester, Shimazu Autograph 200 from Shimazu Corp., when the stretching rate and the distance between the chucks were 300% and 100 mm, respectively.

Measurement

Porosity, Pore Size, and Specific Surface Area. Porosity, pore size, specific surface area were measured by using an Hg porosimeter, Poresizer and 9310, from Shimazu Corp.

N₂ 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



Figure 1 Transmission electron micrographs of sample (A) and sample (B).

| Sample | Thickness | Monomer Unit Content | Porosity | Pore Size | Specific Surface |
|--------|--------------|---|-------------|-----------------|------------------|
| | (mm) | (Wt %) | (%) | (mµ) | Area (m²/g) |
| A B | 0.01 0.01 | $\begin{array}{c} 2.5 \\ 2.1 \end{array}$ | 9.5 10.6 | $\frac{11}{15}$ | 60 38 |

Table II Properties of Microporous PP Films

The stretching ratio is, 3 both in machine and transverse directions, at 160–165°C.

chamber through a pressure regulator. N_2 gas flux was measured at room temperature by a digital flow meter, Model 2500SS, from Sogo Rigaku Industry Co.

respectively. Pretreatment of the sample was carried out with gold ion sputtering for 3 min at 1.2 kV and 8-10 mA.

Transmission Electron Microscopy

The test piece was embedded in an epoxy resin and then treated with RuO_4 for 48 h after trimming. The ultrathin sample was prepared by using an ultramicrotome, a Reichert-Nissei ULTRACUT-N, from Leica AG. The transmission electron microscope was a JEM 200CX from JEOL Ltd.

Scanning Electron Microscopy

The surface and cross section of the microporous PP fiber is observed with the aid of a scanning electron microscope, JSM-220, from JEOL Ltd. The accelerated voltage and the probe current were 15 kV and 5 mA,

RESULTS AND DISCUSSION

Figure 1 shows transmission electron micrographs of the polymer composites containing poly(St-DVB) or poly(GMA-DVB) particles, which support the copolymerization mechanism described above. Microporous PP films are prepared by biaxially stretching the base sheets. The PP phase splits at the periphery of the minute particles. Table II shows some properties of microporous PP films. The pore sizes are very minute, and the specific surface areas are pretty large, although the porosities are rather small. This means that the film textures are very fine. It is very interesting that the microporous PP films are transparent due to the very small size of the polymer particles and the pores. Figure 2 shows N₂ gas fluxs through the film A and film B. The linear relations are obtained in both the cases.



Figure 2 J versus ΔP .



Figure 3 K versus \overline{P} .

| Sample | Finesse Denier | $egin{array}{c} E_b \ (\%) \end{array}$ | TS (kg/cm ²) | YM (kg/cm ²) | Pore Size (µm) | Porosity (%) | Specific Surface Area (m²/g) |
|--------|-------------------|---|---|--|---|-----------------|------------------------------------|
| A B | 90 65 | $\begin{array}{c} 13\\ 15\end{array}$ | $\begin{array}{c} 0.3 \\ 0.5 \end{array}$ | $\begin{array}{c} 3.3\\ 8.1 \end{array}$ | $\begin{array}{c} 0.02\\ 0.01\end{array}$ | $56\\49$ | 106 128 |

Table III Properties of Microporous PP Fibers

Stretching ratio: 9-10.

Also, the N_2 gas permeability coefficients can be estimated by using the following equation:

$$J = \mathbf{K} \,\Delta P l^{-1} \tag{1}$$

where J is the gas flux (cm/s), K is the gas permeability coefficient (cm²/s kg), ΔP is the pressure dif-



Surface



Cross-section

Fiber axis

Figure 4 Scanning electron micrographs of the surface and the cross section of microporous PP fiber [sample (B)].

ference across the sample (kg/cm²), and l is the sample thickness (cm). Figure 3 shows that the linear relations are obtained between K and the mean pressure \bar{P} , and the linear lines do not cross with the ordinate. Accordingly, the pore sizes and the tortuosity factors of pores could not be estimated according to the method by Yasuda et al.¹¹ and Cabasso et al.¹² Furethermore, it means that the pores are very small, as shown in Table II.

Table III shows some properties of microporous PP fibers. The pore sizes are very minute, and the specific surface areas are pretty large. Figure 4 shows scanning electron micrographs of surface and the cross section of the microporous PP fiber (sample B). There are many long eliptical pores parallel to the fiber axis in the surface, and the cross section shows that the microporous PP fiber consists of very fine PP fibrils parallel to the fiber axis and interconnected together, which result from splitting of the PP phase by stretching.

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