Preparation of Microporous Polypropylene Sheets Containing $CaCO_3$ Filler: Effect of Draft Ratio

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SYNOPSIS

Microporous polypropylene sheets were prepared as follows. First, polypropylene pellet-containing $CaCO_3$ filler was extruded to prepare base sheets, which were then biaxially stretched. The draft effect at the extrusion process was studied in relation to some properties of the resultant microporous polypropylene sheets. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Microporous membranes, films, and sheets are prepared by various methods.[1,2] We also reported on microporous polypropylene (PP) sheets containing $CaCO_3$ fillers,[3-6] which are prepared by biaxially stretching PP sheets containing $CaCO_3$ fillers (base sheet). At the extrusion process to prepare the base sheets, the molten PP composite is extruded, and orientation of PP molecules would occur to some extent. It could be presumed that the draft ratio would affect the structure and properties of the resultant microporous PP sheets. Then, we studied the effect of the draft ratio to some properties of microporous PP sheets: porosity, Gurley's air permeability, maximum pore size, and water vapor permeability, and some details are reported in this article.

EXPERIMENTAL

Materials

PP powder was PN-120 (MFI, 1.2) from Tokuyama Corp. $CaCO_3$ filler was of commercial grade (particle size, 0.08 μm in diameter). Polybutadiene was GI-1000 from Nippon Soda Co., and 2,6-di-*t*-butyl-4-methylphenol of commercial grade was used as an antioxidant.

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Preparative Procedure

PP powder (40 wt %), $CaCO_3$ filler (60 wt %), polybutadiene (2 wt % of $CaCO_3$ filler), and the antioxidant (1.3 wt % of PP powder), were well mixed in advance. Then, the mixture was extruded at 230°C to prepare a pellet containing the $CaCO_3$ filler by using an extruder with twine screws. Subsequently, the base sheets were molded at 230°C by extruding the PP composite pellet through a flat die with a lip 1.2 mm wide and 400 mm long, and cooled by using a chilling roll. First, the base sheets were stretched in machine direction (MD; stretching ratio, 5.5), fixing the base sheets to keep their width constant. Next, the resultant sheets were stretched in transverse direction (TD).

Measurement

Porosity

Apparent specific gravities of the base sheet (d_0, g/cm^3) and the microporous sheet (d, g/cm^3) were estimated by the buoyancy method in water, and porosity of the microporous sheet was calculated by using the following equation:

$$\text{Porosity (\%)} = (d_0 - d)/d_0 \quad (1)$$

Maximum Pore Size

Maximum pore size was estimated by the methanol bubble-point method, using the following equation (ASTM F-316):

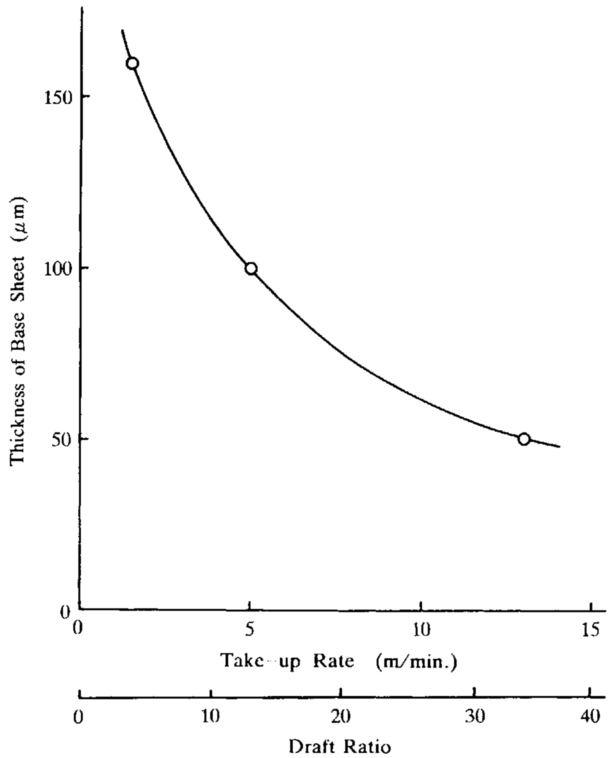

Figure 1 Thickness of base sheet vs. take-up rate and draft ratio.

$$\text{Maximum pore size } (\mu m) = 0.9388/P \quad (2)$$

where P is the N_2 gas pressure (kg/cm^2), when three continuous bubbles appeared from the sample surface.

Gurley's Air Permeability

Gurley's air permeability is defined as the time during which 100 ml of air permeates through microporous sheets (effective area, 6.168 cm^2) (JIS P-8117).

Water Vapor Permeability

A sample was tightly set on a cup containing anhydrous $CaCl_2$ granules and it was kept at 25°C under relative humidity of 90% for 24 h. The weight increase is defined as water vapor permeability (g/m^2/24 h).

Scanning Electron Microscopy

The surface and cross-section of the microporous PP sheet were observed with the aid of an electron microscope, JSM-220 from JEOL Ltd. The accelerated voltage and the probe current were 15 kV and 5 mA, respectively. Pretreatment of each sample was carried out with gold ion sputtering for 3 min at 1.2 kV, and 8 ~ 10 mA.

RESULTS AND DISCUSSION

The base sheets were prepared by extruding PP pellet-containing $CaCO_3$ filler through the flat die. At this process, the thickness of the base sheets is adjustable by controlling the take-up rate of the sheets.

Figure 1 shows the relation between the thickness of the sheet and the take-up rate; draft ratio, in other words. The thickness reasonably decreases with increasing the draft ratio. Here, the extruded PP composite is pulled, depending on the draft ratio. It suggests that PP molecular chains are probably oriented to some extent in MD direction. Then, the orientation degree would be affected by the draft ratio. The details are obscure now. It is presumed that the real situation is rather complex. Accordingly, we investigated the effect of the draft ratio to some properties of microporous, PP sheets after biaxial stretching.

The base sheets were successively stretched in MD and TD directions. Figure 2 shows the thickness changes of microporous PP sheets by stretching in

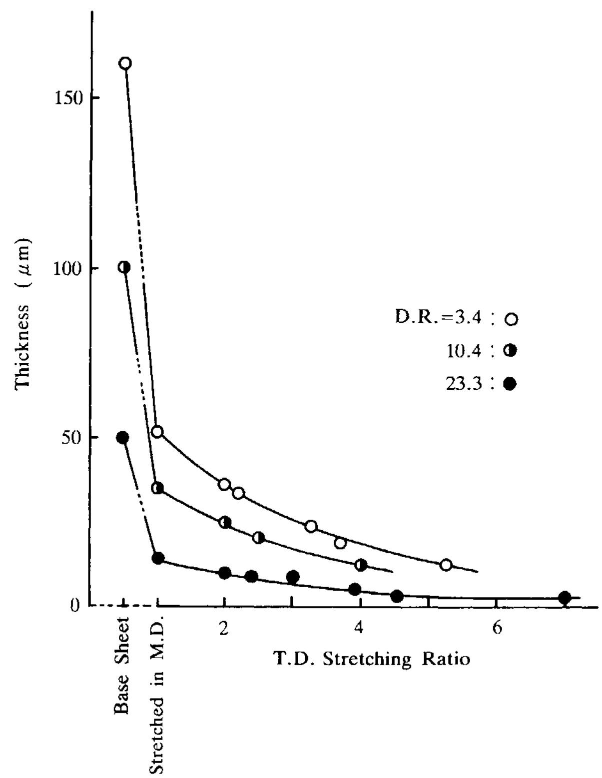

Figure 2 Thickness of sheet vs. TD stretching ratio.

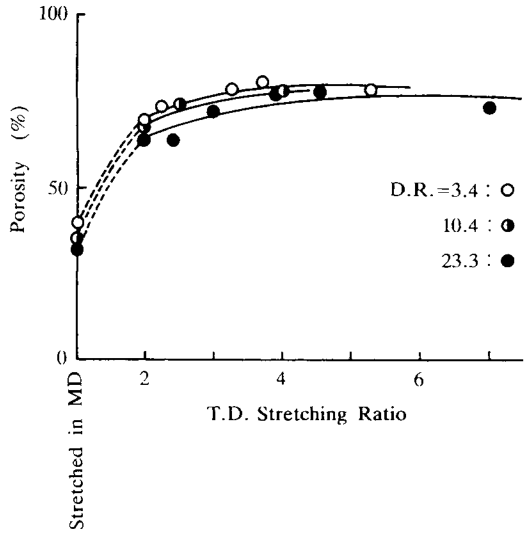

Figure 3 Porosity vs. TD stretching ratio.

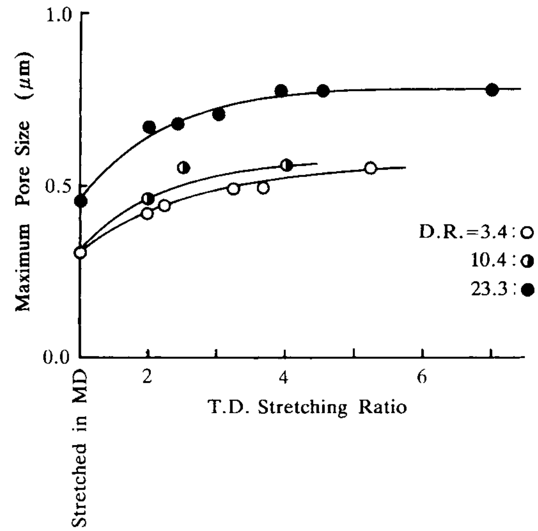

Figure 4 Maximum pore size vs. TD stretching ratio.

MD and TD directions. First, the sheet thickness drastically decreases by MD stretching, and then gradually decreases by TD stretching. Reasonably, the thickness decreases with increasing TD stretching ratio, and the larger the draft ratio, the thinner the resultant sheet at the same TD stretching ratio. It is interesting that, regarding the draft ratio, the difference in the thickness becomes smaller with increasing TD stretching ratio.

Figure 3 shows effect of TD stretching ratio to porosity of microporous PP sheets in relation to the draft ratio. With increasing the TD stretching ratio, the porosity increases at first, and then attains a definite value. The differences in the porosities are small in relation to the draft ratio, and the smaller the draft ratio, the thicker the sheet; in other words, the larger the porosity. Presumably, the participation of not only the orientation of the PP molecular chain, but skin layers on the sheet surfaces, could be considered, but the details are still obscure.

Figure 4 shows the relation between maximum pore size of microporous PP sheets and TD stretching ratio in relation to the draft ratio. Maximum pore sizes gradually increase at first and then attain definite values.

In the case of the draft ratio equaling 23.3, the maximum pore sizes are larger than those in the other cases, when the TD stretching ratio is the same. Accordingly, the Gurley's air permeability of microporous PP sheets in the case of the draft ratio equaling 23.3 are smaller than those in the other cases, as shown in Figure 5.

As shown in Figures 3–5, the results show that the draft ratio is affective to the porosity, the maximum pore size, and Gurley's air permeability. However, regarding the estimation of these properties, the sheet thickness is not taken into consideration. Then, we checked it as follows. Figures 6–8 show the effect of the sheet thickness on the porosity, the maximum pore size, and Gurley's air permeability. The porosity is dependent on the sheet

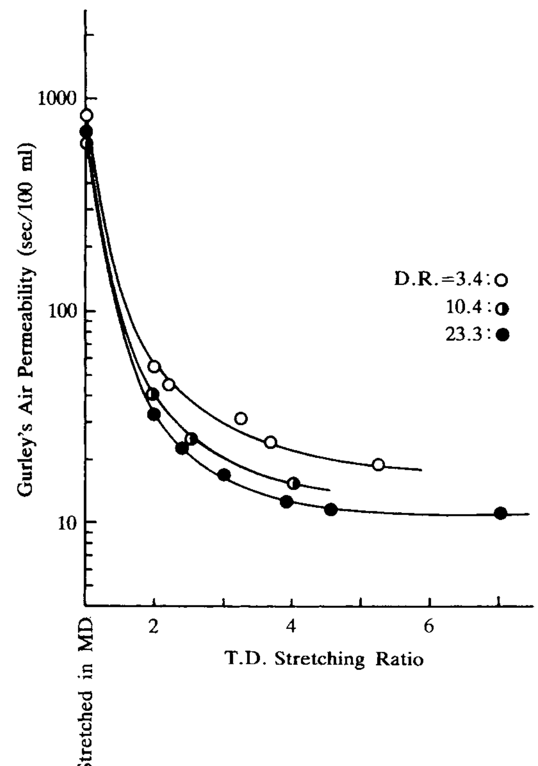

Figure 5 Gurley's air permeability vs. TD stretching ratio.

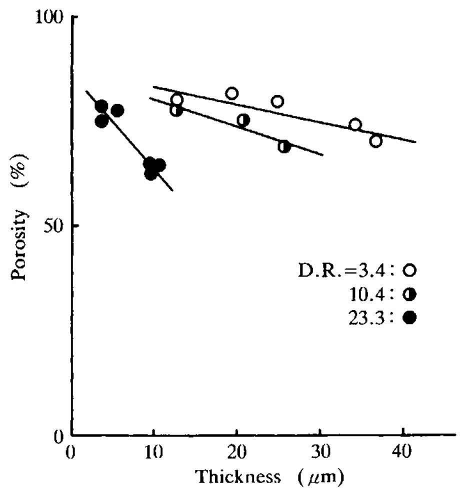

Figure 6 Porosity vs. sheet thickness.

thickness, and also evidently affected by the draft ratio: when the draft ratio is the same, the porosity linearly decreases with increasing the sheet thickness, and also the slope of the linear relation becomes larger with increasing the draft ratio (Fig. 6).

Similar tendencies are elucidated regarding the maximum pore size (Fig. 7). Figure 8 shows dependencies of Gurley's air permeability on the sheet thickness. Reasonably, the Gurley's air permeability linearly increases with increasing the sheet thickness in all the cases of the draft ratio. As described above, it is suggested that the draft ratio affects the structure of the base sheet by altering the orientation of the PP molecular chain and formation of skin layers on the sheet surfaces. Then, the draft ratio is concerned with formation of the fibrous texture of microporous PP sheets by MD, and subsequent TD, stretching. On the other hand, the crystallinity of

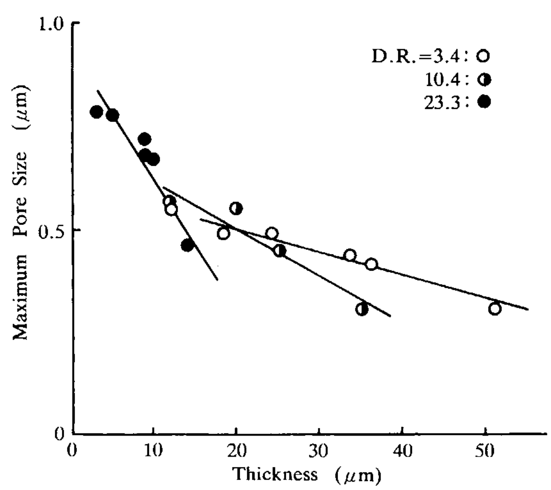

Figure 7 Maximum pore size vs. sheet thickness.

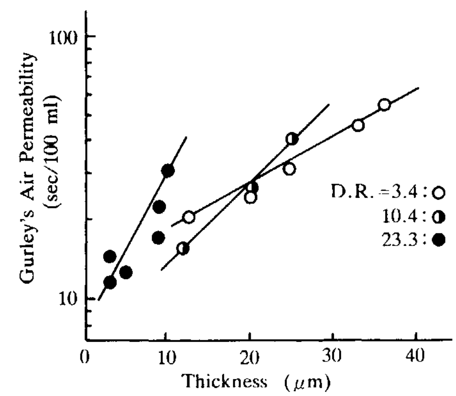

Figure 8 Gurley's air permeability vs. sheet thickness.

microporous PP sheets is not affected by the stretching ratio: 53 ~ 60% after MD stretching and about 60% after subsequent TD stretching.[6]

Figure 9 shows the effect of TD stretching ratio to water vapor permeability of microporous PP sheets in relation to draft ratio. It is interesting that not only the TD stretching ratio, but also the draft ratio, apparently do not affect the water vapor permeability. Probably, it is attributable to the hydrophobic character of the microporous PP sheets, but the details are obscure.

CONCLUSION

Microporous polypropylene sheets are prepared by extruding polypropylene pellets containing $CaCO_3$ filler to prepare the base sheets and, subsequently, by biaxially stretching the base sheets. It is elucidated that the draft ratio at the extrusion process

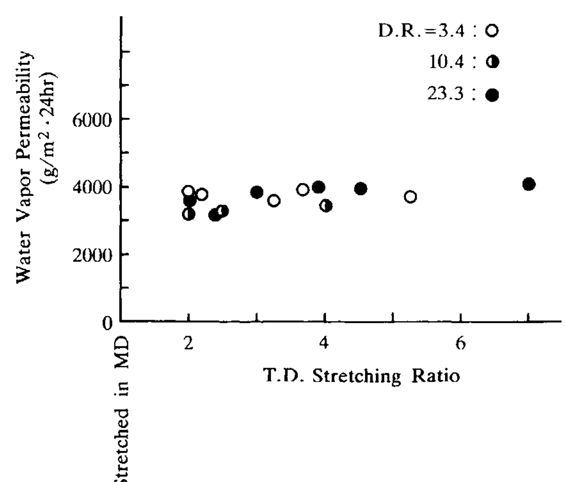

Figure 9 Water vapor permeability vs. TD stretching ratio.

delicately affects porosity, maximum pore size, and Gurley's air permeability of the resultant microporous PP sheets. It is presumed that the draft ratio is a factor in relation to some orientation of the PP molecular chain, and also formation of skin layers at the extrusion process, and results in the delicate difference in the fibrous texture of the microporous sheets. The details should be studied further.

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