Microporous Polypropylene Fibers Containing Poly(methylsilsesquioxane) Filler

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SYNOPSIS

Microporous polypropylene fibers were prepared by stretching polypropylene fibers containing poly(methylsilsesquioxane) filler. The properties of the resultant fibers are controllable by adjusting the filler content and stretching degree. The resultant fibers have a fine texture of polypropylene fibrils, in which the filler particles are dispersed. Some properties were investigated: tensile strength, elongation, Young's modulus, porosity, pore size, and specific surface area. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

We reported the preparative methods of microporous polypropylene (PP) sheets and hollow fibers containing poly(methylsilsesquioxane) (PMSO) fillers. The former is prepared by biaxially stretching PP sheets containing the fillers[1] and the latter is prepared by monoaxially stretching PP microtubes containing the fillers.[2,3]

In this article, we report preparation and some properties of microporous PP fibers.

EXPERIMENTAL

Materials

PP powder was PN-150 [melt flow index (MFI), 16g/ 10 min] from Tokuyama Corp. PMSO filler with uniform particle size was from Toshiba Silicone Co, Ltd and the particle size was 0.3 μm. Polybutadiene (GI-1000 from Nihon Soda Co, Ltd) and 2,6-di-t-butyl-4-methylphenol were used as an additive and an antioxidant, respectively.

Preparative Procedure

PP powder, PMSO filler, the antioxidant, and the additives were well mixed in advance and then ex-

truded at 230°C to prepare the pellet. The resultant pellet was extruded at 200–290°C through the dies, of which the spinneret number and size were 198 and 0.7 mm in diameter, respectively.

The obtained fiber was stretched at 150°C with the aid of seven Godet rolls. The amount of polybutadiene and 2,6-di-t-butyl-4-methylphenol were 0.7% and 1.3% of the filler and PP, respectively.

Measurement

Mechanical Properties

Tensile strength at yield (TS), Young's modulus (YM), and elongation to break (Eb) were measured at 20 ± 1°C with the aid of a tensile tester, Shimazu Autograph 200 from Shimazu Corp, when stretching rate and distance between chucks were 300%/min and 100 mm, respectively.

Porosity, Pore Size, and Specific Surface Area

Porosity, average pore size, and specific surface area were measured with the aid of an Hg porosimeter, Poresizer 9310, from Shimazu Corp.

Scanning Electron Microscopy

The texture of the microporous PP fibers was 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, respectively. Pretreatment of each sample was car-

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ried out with gold ion sputtering for 3 min at 1.2 kV and 8–10 mA.

RESULTS AND DISCUSSION

Microporous PP fibers were prepared by stretching PP fibers containing PMSO fillers. The stretching causes splitting of the PP phase at the periphery of the filler particles and results in a microporous texture of PP fibrils. Therefore, the filler content, the particle size of filler, and the stretching ratio affect the resultant fibrous texture. Here, it is reasonable to presume that the use of PMSO filler with relatively smaller particle size is preferred to prepare relatively finer microporous PP fiber, and it was elucidated that PP pellets containing PMSO filler can be spinnable, of which the content of the upper limit is 35%. This fact is beyond anticipation and is ascribed to sphericity of the PMSO filler particles with relatively less cohesive tendency. For

reference, the upper limit of the filler content is about 25% in the case of $CaCO_3$ filler with particle size of 0.09 μm.[4]

Figure 1 shows scanning electron micrographs of surfaces and cross-sections of microporous PP fibers. Evidently, finely split PP textures can be observed. There are long elliptical pores on the surfaces, parallel to the fiber axis, and PMSO filler particles are dispersed in the fibrous texture of PP. These pictures support the results described before.
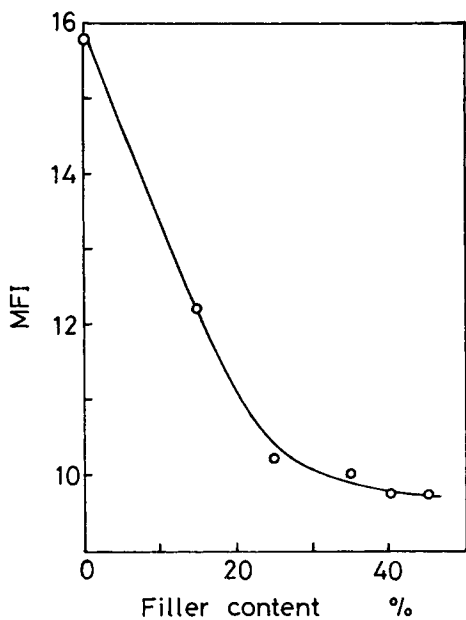
Figure 2 shows relation of PMSO filler content to MFI of PP-PMSO filler composite. MFI reasonably decreases with increasing the filler content.

Figure 3 shows dependency of fineness of spun fibers, which are not stretched yet, onto draft ratio. The resultant fibers become finer with increasing draft ratio. At this process, the molten PP composite is extruded through spinneret, pulled, and cooled by air to be taken up.
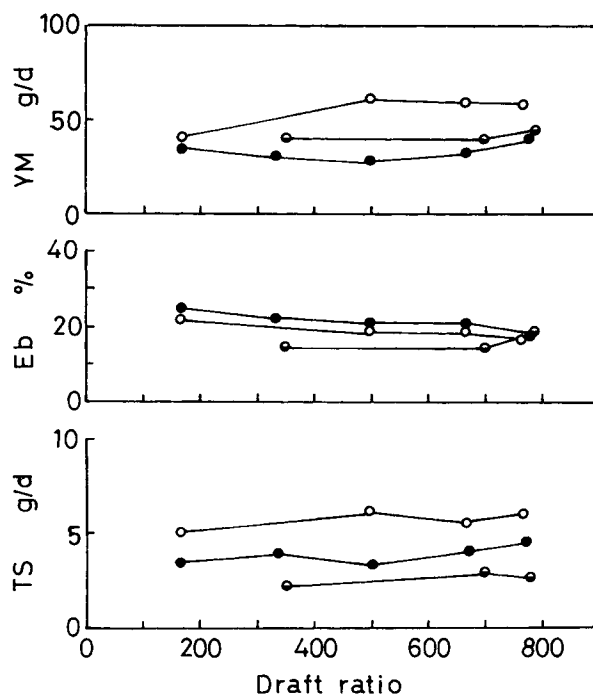
Accordingly, PP molecular chains are orientated to some extent in the direction of fiber axis, depending on draft ratio. However, the details of the
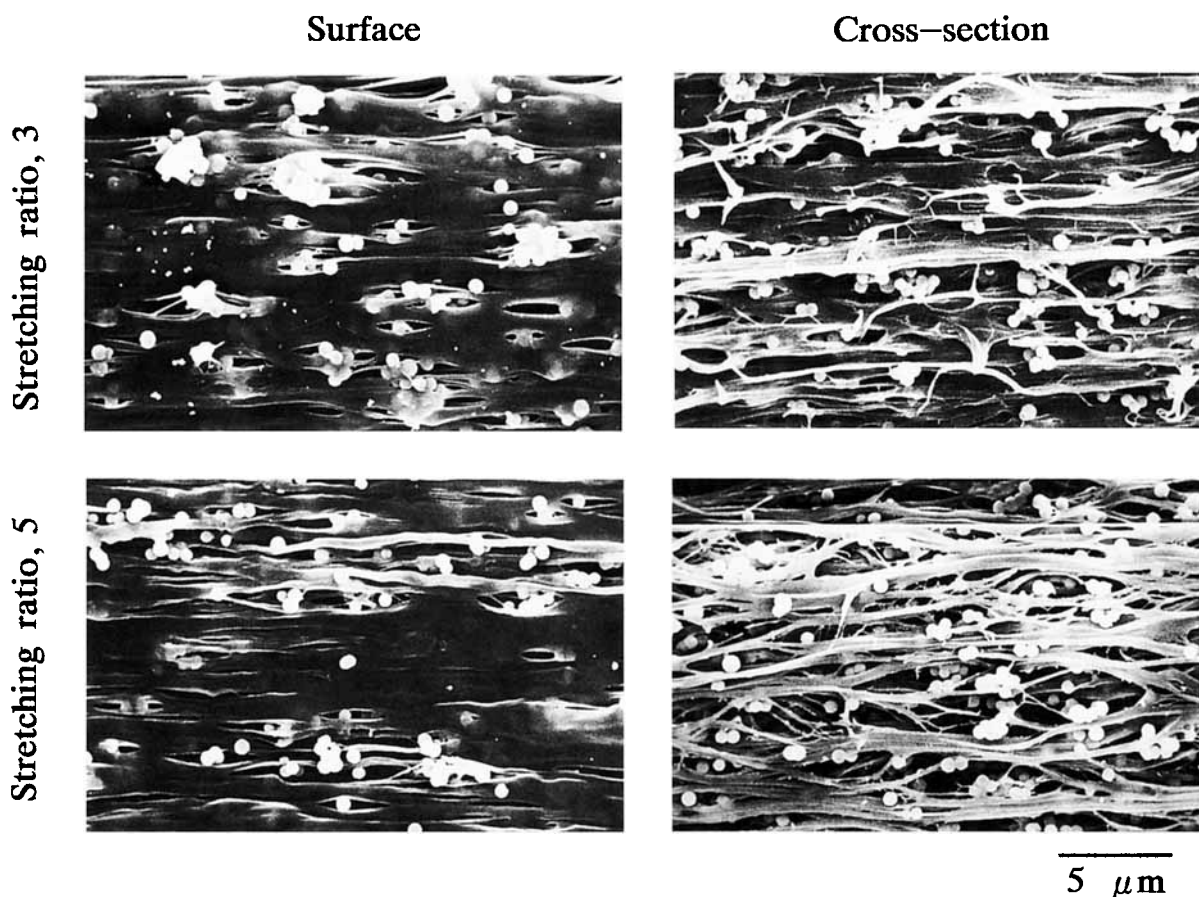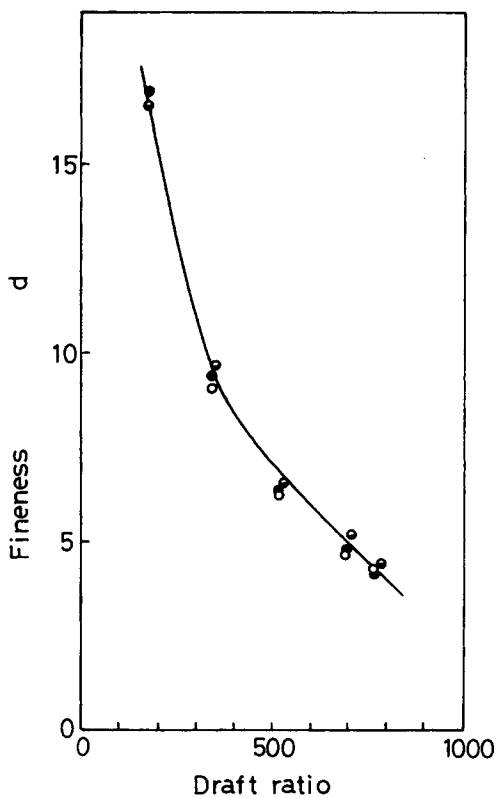

Figure 1 Scanning electron micrographs of surfaces and cross-sections of microporous PP fibers.
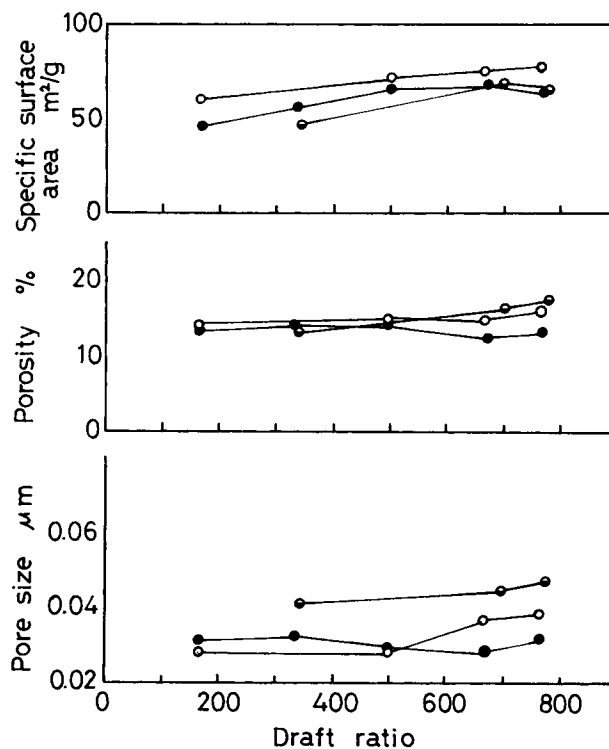
Figure 2 Relation of PMSO filler content to MFI of PP-PMSO filler composite.

Figure 3 Dependency of fineness of spun fibers onto draft ratio.

Figure 4 Effect of draft ratio to TS, Eb, and YM of stretched fibers. O, filler content, 15% and stretching ratio, 5; ●, filler content, 25% and stretching ratio, 4; and ◖, filler content, 35% and stretching ratio, 4.

Figure 5 Effect of draft ratio to pore size, porosity, and specific surface area of stretched fibers. The symbols are same as those shown in Figure 3.
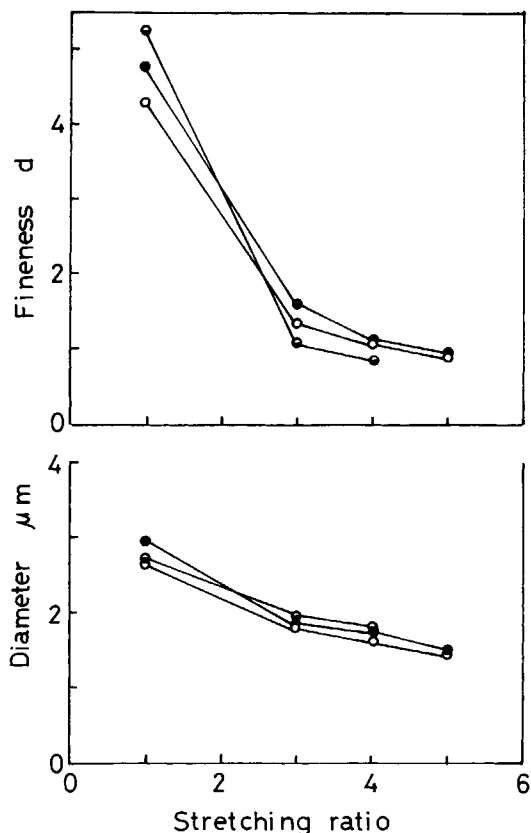
Figure 6 Changes in diameter and fineness of microporous PP fibers by stretching. The symbols are same as those shown in Figure 3.

orientation in the presence of pretty large amount of PMSO filler particles are still obscure. Also, the draft ratio was ineffective to crystallinity of the spun fibers (44–45%, determined by X-ray diffraction).

Effect of Draft Ratio

The orientation of PP molecular chains is presumed to be effective to the splitting of PP phase by stretching at periphery of the filler particles.

Figure 4 shows effect of draft ratio to TS, Eb, and YM of the stretched fibers. Here, it is noteworthy that PMSO filler content directly relates to PP phase content, which is split and stretched. Accordingly, the fibers containing relatively less PMSO filler could have relatively better properties. The obtained results support this presumption, especially considering the cases when the stretching ratio is 5 and the PMSO filler content is 15%. As a whole, draft ratio is ineffective to mechanical properties of the resultant microporous PP fiber.

Figure 5 shows the effect of draft ratio on microporous texture of the fibers. It seems that draft ratio

is not so effective on pore size, porosity, and specific surface area, but the pore sizes are minute and the specific surface area are large, although the porosity is not so large. This probably suggests the compactness of the finely fibrous texture.

Figures 6 shows changes in diameter and fineness of the microporous PP fibers by stretching. Here, we used the unstretched fibers (stretching ratio 1) prepared by relatively similar draft ratios. Both the diameter and fineness become similar with increased stretching ratio. It is interesting that the changes of diameters are apparently smaller than those of fineness shown by denier. The decrease of the fineness is due to the formation of the microporous texture; on the other hand, PMSO filler particles play a role as a spacer regarding the changes of the diameters. Also, the stretching ratio was ineffective to crystallinity of the microporous PP fibers (about 47%, determined by X-ray diffraction).

Figure 7 shows dependencies of mechanical properties of the microporous PP fibers on the stretching ratios. TS and YM increase a little with increased stretching ratio and Eb contrarily decreases.

These tendencies are similar to those of ordinary PP fibers,[5,6] but the details should be studied further. Figure 8 shows the effect of stretching ratio on microporous texture of the fiber. The pore size, the
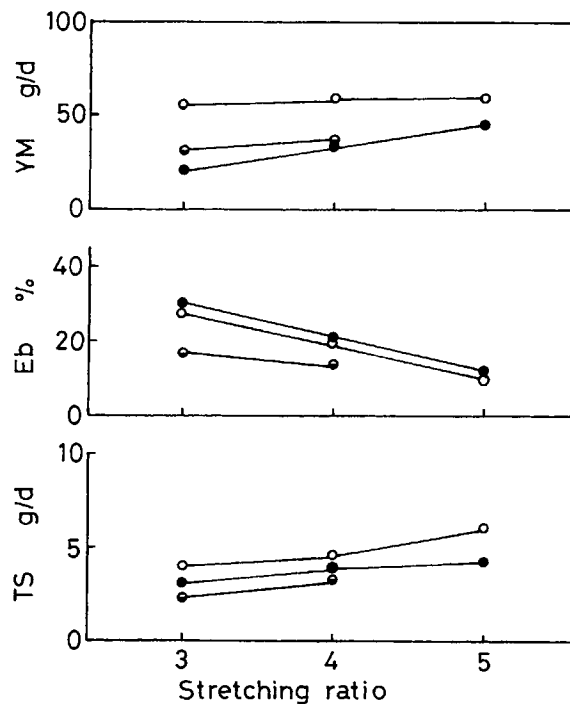
Figure 7 Dependencies of TS, Eb, and YM of microporous PP fibers on stretching ratio. The symbols are same as shown in Figure 3.
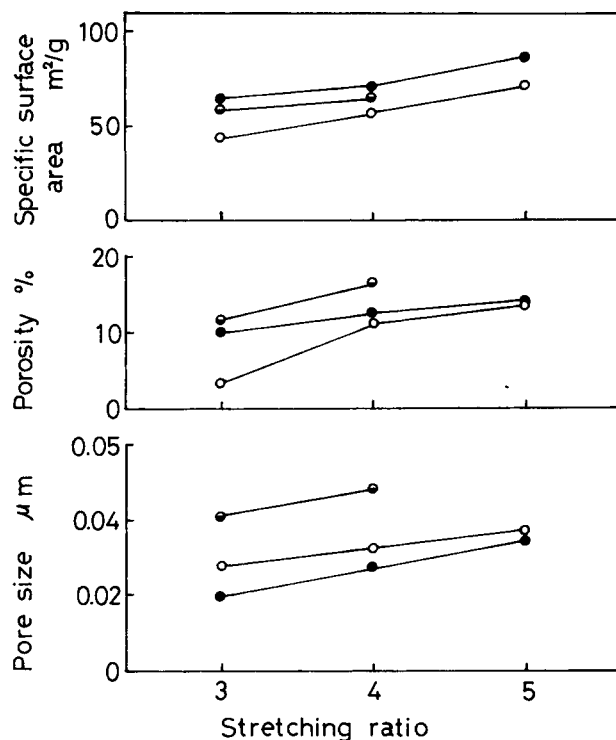
Figure 8 Dependencies of pore size, porosity, and specific surface area on stretching ratio. The symbols are same as those shown in Figure 3.

porosity, and the specific surface area increase with increased stretching ratio. These results mean that the larger the stretching ratio, the more microporous the PP fiber texture. Therefore, it is concluded that the stretching is the dominant factor regarding the formation of microporous texture consisting of fibrous PP and PMSO filler particles, and the filler

content is also the other important factor. It is interesting that the pore size is very minute (0.02–0.05 μm) and the specific surface area is pretty large (40–90 m^2/g). For reference, in the case of microporous PP fibers containing CaCO$_3$ filler (particle size, 0.09 μm; content, 25%), pore size and specific surface area are 0.01–0.02 μm and 10–120 m^2/g, respectively, depending on stretching ratio (3–5).[4]

CONCLUSION

Microporous PP fibers are prepared by stretching PP fibers containing PMSO filler. Their pore sizes and specific surface areas are 0.02–0.05 μm and 40–90 m^2/g, respectively. Also, mechanical properties are in the applicable range. Accordingly, their practical applicability should be investigated further.

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