Microporous Polypropylene Fibers Containing $CaCO_3$ Fillers

SATOSHI NAGÓ* and YUKIO MIZUTANI

Tokuyama Corp, Tokuyama-City, 745 Japan

SYNOPSIS

Microporous polypropylene fibers were prepared by stretching polypropylene fibers containing $CaCO_3$ filler. The properties of the resultant fibers are controllable by adjusting the filler content and the stretching ratio. Also, it is elucidated that the fibers have a fine texture of polypropylene fibrils, in which the filler particles are dispersed. Furthermore, the $CaCO_3$ filler was removed by treating the fibers with an HCl–CH_3OH solution, and their properties were also investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Many investigators have studied microporous materials (film, membrane, hollow fiber, and fiber) as key materials for separation technology.[1-5] On the other hand, we reported the preparative methods of microporous polypropylene (PP) sheets[6-8] and hollow fibers.[9-12] The microporous PP sheets are prepared by biaxially stretching PP sheets containing $CaCO_3$ or polymethylsilsesquioxane fillers, and the microporous PP hollow fibers are prepared by monoaxially stretching PP microtubes containing the fillers described above.

In this article, we report the preparation of microporous PP fibers by stretching PP fibers containing $CaCO_3$ filler, extending the methods described above. Also, the $CaCO_3$ filler was removed by treating the fibers with an HCl–CH_3OH solution, and some properties of the resultant fibers were also investigated.

EXPERIMENTAL

Materials

PP powder was PN-150 [melt flow index (MFI), 16 g/10 min] from Tokuyama Corp. $CaCO_3$ filler was of commercial grade (particle size, 0.09 μm in diameter). Polybutadiene was GI-1000 from Nippon Soda Co. Antioxidant was 2,6-di-*t*-butyl-4-methylphenol.

Preparative Procedure

PP powder (75 wt %), $CaCO_3$ filler (25 wt %), and the additives were well mixed in advance and then extruded 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 its diameter were 198 and 0.7 mm, respectively. The obtained fiber was stretched at 150°C with the aid of seven Godet rolls. The amounts of polybutadiene and the antioxidant were 0.7 and 1.2% of the filler and PP, respectively.

HCl-CH_3OH Treatment

Microporous PP fiber was dipped into a mixture of 1*N* HCl–CH_3OH (1 : 1 by volume) at room temperature for 8 h with stirring.

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 the stretching rate and the distance between the chucks were 300%/min and 100 mm, respectively.

Porosity, Pore Size, and Specific Surface Area

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

* To whom correspondence should be addressed.

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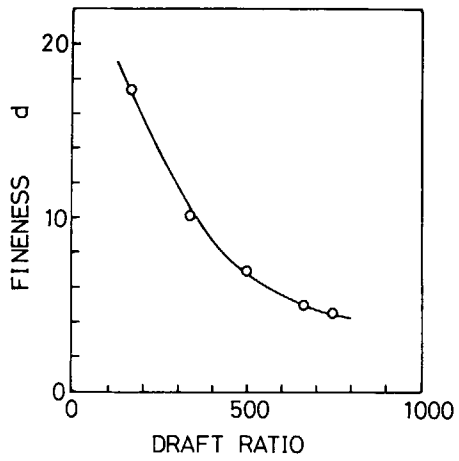

Figure 1 Effect of draft ratio to fiber fineness before stretching.

Scanning Electron Microscopy

The texture of microporous PP fibers was observed by using a scanning electron microscope, JSM-220 from JEOL Ltd. The accelated voltage and the probe current were 15 kV and 5 mA, respectively. 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

Microporous PP fibers are prepared by stretching PP fibers containing $CaCO_3$ filler. The stretching causes splitting of the PP phase at the periphery of the filler particles and results in a microporous PP texture, which is the reason for whitening of the resultant fibers. Therefore, the filler content, the particle size of the filler, the draft ratio, and the stretching ratio affect the properties of microporous PP fibers. Here, we used $CaCO_3$ filler with relatively smaller particle size (0.09 μm in diameter) to prepare relatively finer fibers. Also, we preliminarily confirmed that the appropriate filler content is 25 wt %, because when the filler content is 35 wt %, long-lasting spinning is hardly carried out because of choking of the mesh attached in the extruder by the aggregated filler particles.

Figure 1 shows relation between draft ratio and fineness of spun fiber. Reasonably, the larger the draft ratio, the finer the fiber. Subsequently, the spun fibers were stretched to make the fibers microporous. Table I shows the stretching effect on the fiber fineness and also the effect of the HCl–CH_3OH treatment to remove the $CaCO_3$ filler.

The diameter does not change substantially and the denier value decreases with increasing the stretching ratio. It comes from the increase of the fiber porosity as described later. The fibers become finer by the HCl–CH_3OH treatment, probably owing to loss of the $CaCO_3$ filler particles as a spacer for the PP fibrils. Table II shows some changes of the fiber properties by the HCl–CH_3OH treatment, which remove 38–45% of the $CaCO_3$ filler. It is interesting that the fibers shrink a little: the larger the stretching ratio, the less the amount of $CaCO_3$ filler is removed and the more the fiber shrinks. This result supports not only the role of the filler particles as the spacer but the fact that the diameter after the HCl–CH_3OH treatment is not affected by the stretching ratio (Table I).

Effect of Draft Ratio

At the spinning process, the extruded PP composite is extended and cooled by air. Then, PP molecules are oriented to some extent in the direction of the fiber axis even in the presence of the filler particles. Therefore, it is presumed that draft ratio affects mechanical properties and texture of the stretched fibers.

Figure 2 shows dependencies of Eb, TS, and YM of the stretched fibers on the draft ratio, when the

Table I Stretching Effect on Fiber Fineness

	Diameter (μm)		Denier (d)	
Stretching Ratio	No Treatment	HCl–CH_3OH Treatment	No Treatment	HCl–CH_3OH Treatment
3	2.0	1.7	1.4	1.3
4	1.9	1.7	1.3	1.2
5	1.9	1.7	1.1	1.1

Unstretched fiber: diameter 3.0 μm and fineness 5.7 d.

Table II Effect of HCl–CH_3OH Treatment on the Fibers

Stretching Ratio	$CaCO_3$ Content[a] (w_1, g)	Decrease in Weight (w_2, g)	w_2/w_1	Shrinkage in Length (%)
3	0.078	0.035	0.45	0.5
4	0.070	0.031	0.44	1
5	0.065	0.025	0.38	3

[a] Calculated by (fiber weight) × ($CaCO_3$ filler content in the recipe).

stretching ratio was 5. TS values before and after the HCl–CH_3OH treatment are not affected by the draft ratio. On the other hand, YM values slightly increase with increased draft ratio and Eb values show a maximum at a draft ratio of 670. It is elucidated that the draft ratio is ineffective to the crystallinity of the resultant unstretched fibers, as shown in Table III, but the details of the orientation of PP molecules in the presence of $CaCO_3$ filler particles are obscure. Accordingly, the tendencies described above are inexplicable now. However, it is interesting that all values of the fibers after the treatment are larger than those before. It is probably attributable to the removal of $CaCO_3$ filler particles as the spacer among PP fibrils.

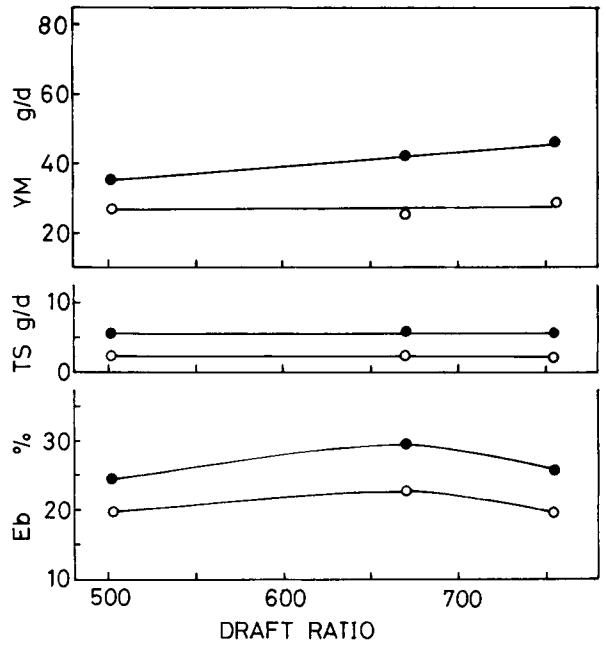

Figure 2 Effect of draft ratio to mechanical properties of stretched fibers. Stretching ratio, 5; (○) no treatment; (●) after HCl–CH_3OH treatment.

Figure 3 shows dependencies of pore size, porosity, and specific surface area of the stretched fibers on the draft ratio, when the stretching ratio was 5. The draft ratio is rather ineffective on the pore size and the porosity. Here, it is outstanding that the pore sizes are very minute and the specific surface area is large. Also, the specific surface area increases with increased draft ratio. It is presumed that when the draft ratio is larger, the resultant fibers are more easily splittable, resulting in a finer fibrous texture by stretching. Also, the difference between the values of the fibers before and after the HCl–CH_3OH treatment are probably attributable to the removal of $CaCO_3$ filler particles, but the details are still obscure.

Effect of Stretching Ratio

Figure 4 shows dependencies of Eb, TS, and YM of microporous PP fibers on the stretching ratio. Here, it is noteworthy that the real stretching ratio should be larger than the apparent one, because of the presence of $CaCO_3$ filler particles, which should hinder the straight stretching of PP molecules in the direction of the fiber axis.

The stretching ratio is ineffective to TS values of the fibers both before and after the HCl–CH_3OH treatment. Eb values decrease with increased stretching ratio, and YM values do not increase with

Table III Effect of Draft Ratio to Crystallinity of Spun Fibers

	Draft Ratio				
	168	335	502	670	745
Crystallinity[a] (%)	52	53	53	52	53

[a] Determined with the aid of X-ray spectrometer. RU-200B from Rigaku Denki Corp, rotating the sample disk (92 rpm).

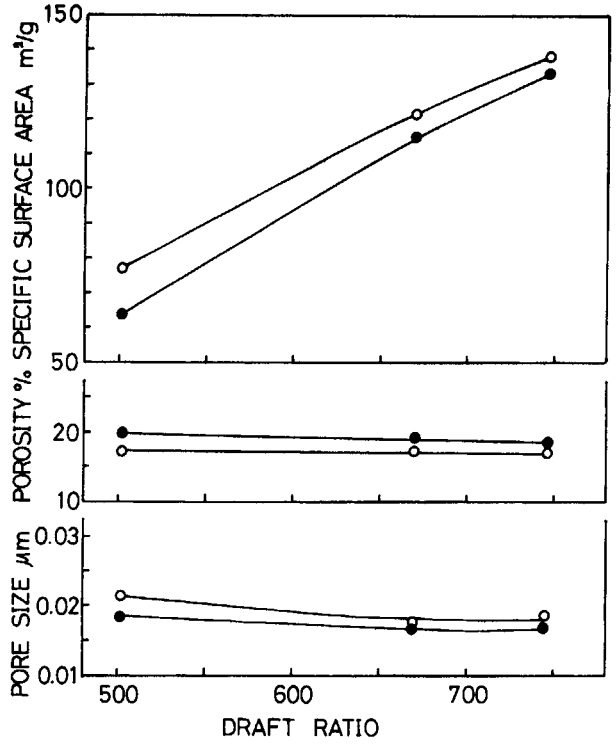

Figure 3 Effect of draft ratio to fibrous texture of stretched fibers. Stretching ratio, 5; (○) no treatment; (●) after HCl–CH_3OH treatment.

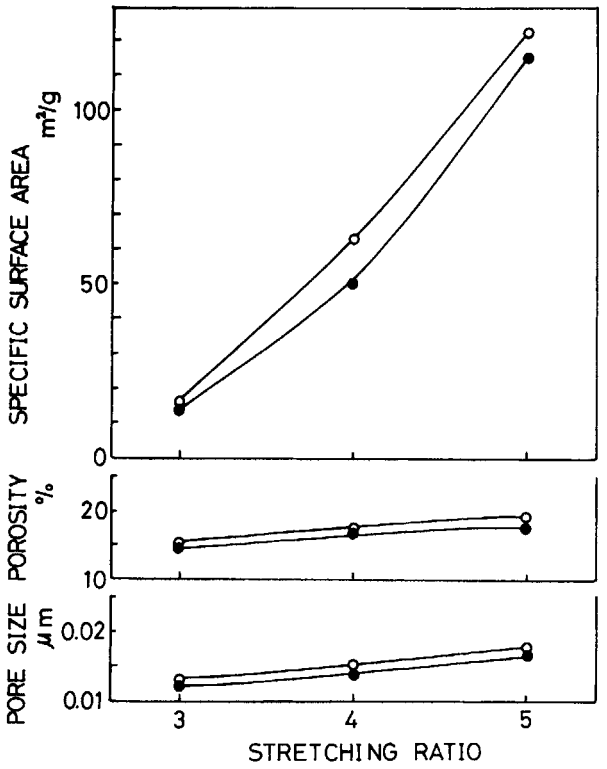

Figure 5 Effect of stretching ratio to fibrous texture of stretched fibers. Draft ratio, 670; (○) no treatment; (●) after HCl–CH_3OH treatment.

increased stretching ratio. Generally in the case of PP fibers, YM and TS values increase and Eb value decreases with increased stretching ratio.[13,14] However, the results of TS and YM are inconsistent with the general tendencies, and it comes from the structural difference between ordinary fibers and the microporous fibers with the fibrous PP texture. Also, all values of the fibers after the HCl–CH_3OH treatment are larger than those before, and its reason is obscure now.

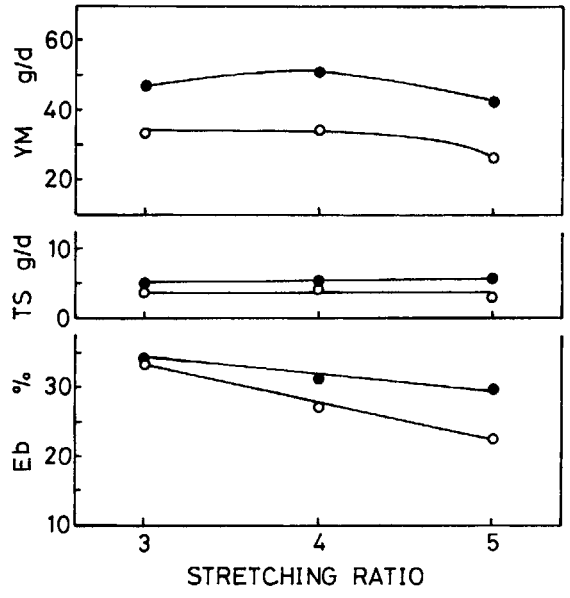

Figure 4 Effect of stretching ratio to mechanical properties. Draft ratio, 670; (○) no treatment; (●) after HCl–CH_3OH treatment.

Figure 5 shows dependencies of pore size, porosity, and specific surface area on the stretching ratio. They increase with increased stretching ratio. These very minute pore sizes and large specific surface areas suggest that the fibrous textures of the fibers are very fine, especially considering not so large porosity. The difference between all values of the fibers before and after the HCl–CH_3OH treatment is be-

Table IV Stretching Effect to Crystallinity of Fibers

	Stretching Ratio		
	3	4	5
Crystallinity (%)	60	56	52

Draft ratio, 670.

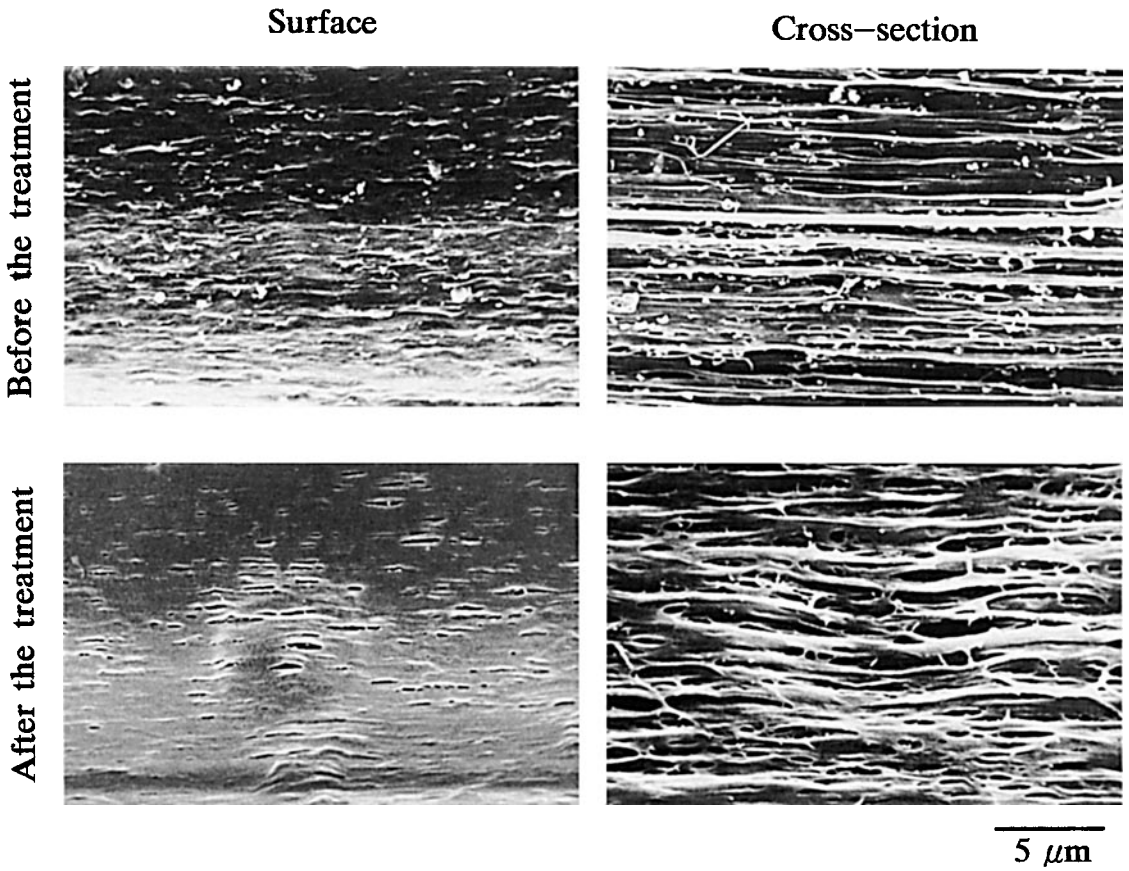

Figure 6 Scanning electron micrographs of microporous PP fibers. Draft ratio, 670; stretching ratio, 5.

cause of the shrinkage of the fibers by the treatment to remove $CaCO_3$ filler.

Table IV shows stretching effect to crystallinity of microporous PP fibers. Crystallinity decreases with increased stretching ratio, and this is consistent with general tendency of ordinary PP fibers.[13] For reference, crystallinity of microporous PP sheets containing $CaCO_3$ filler are 55–60% after stretching in machine direction and about 60% after subsequent stretching in transverse direction.[7]

Scanning Electron Microscopy

Figure 6 shows scanning electron micrographs of surfaces and cross sections of microporous PP fibers. The PP phase is split in the direction of the fiber axis to form very fine fibrous texture, as shown in the cross sections. On the other hand, there are very fine slits on the surfaces. These pictures support that the average pore sizes are very small as shown in Figures 3 and 5. Seemingly, the surfaces show that the larger the stretching ratio, the more the split.

CONCLUSION

Microporous PP fibers are prepared by stretching PP fibers containing $CaCO_3$ filler, which is removable by treating with a $HCl–CH_3OH$ solution. Then, we investigated the mechanical properties and the fine fibrous texture of both the fibers before and after the $HCl–CH_3OH$ treatment. The mechanical properties of the microporous PP fibers show different dependencies onto the stretching ratio from those of ordinary PP fibers. It is also elucidated that the pore sizes are very minute and the specific surface areas are large. The practical application should be studied from now on.

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