Microporous Polypropylene Fibers Containing Fine Particles of Poly(glycidylmethacrylate-*co*-divinylbenzene)

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ABSTRACT: Glycidylmethacrylate and divinylbenzene were copolymerized in a *n*-hexane solution of poly(propylene-*co*-1-butene). The resultant polymer composite contains fine particles of poly(glycidylmethacrylate-*co*-divinyl benzene). This composite was blended with polypropylene. Next, the resultant polypropylene composites were melt spun and stretched. Microporous polypropylene fibers were thus prepared and their properties were evaluated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1549–1553, 1999

Key words: microporous polypropylene fiber; poly(glycidylmethacrylate-*co*-divinylbenzene); uniaxially stretching; microporous structure; mechanical properties

INTRODUCTION

We reported that microporous polypropylene (PP) fibers are prepared by stretching PP fibers containing CaCO₃ or poly(methylsilsesquioxane) fillers.^{1,2} In these cases, PP phase is detouched and/or split at the periphery of the filler particles by stretching at the early stage, and further stretching results in a microporous structure. Here, the important factors are the filler content, the size of the filler particles, and the stretching degree. The filler with a relatively smaller particle size is preferable to prepare microporous PP fibers with a relatively smaller pore size. However, the smaller the filler particles, the much more the filler particles tend to aggregate in general. Therefore, there is a limit to the practical smallest pore size achievable due to the aggregated particle size.

On the other hand, Mizutani et al. reported that copolymerization of glycidylmethacrylate (GMA) and divinylbenzene (DVB) in cyclohexane as a poor solvent for poly(GMA) results in a fine powder, of which the particles size is of the 0.1- μ m order.³ Also, the powders are bulky and their handling is not as easy as in practical usage, for example, blending with PP. To overcome these drawbacks, we investigated copolymerization of GMA and DVB in an *n*-hexane solution of poly(propylene-*co*-butene) [poly($C'_3-C'_4$)] and the blend of the resultant polymer composite with PP. Furthermore, the PP composites were melt spun and stretched to prepare microporous PP fibers, of which the properties were estimated.

EXPERIMENTAL

Materials

DVB used was of commercial grade (purity, 55%) and all the other reagents used were of chemical grade.

PP powder was PN-120 from Tokuyama Corp. [melt flow index at 230°C under a load of 2.16 kg \cdot f (MFI)], 1.2 g/10 min, and poly(C'₃-C'₄) was Beaulon M-2481 from Mitsui Petrochemical Industries Ltd. (1-butene content, 80 wt %, molecular weight, 260,000, and m.p., 75°C).

Polymerization of GMA and DVB

n-Hexane (300 mL) was put into a separable flask (500 mL) fitted with a thermometer, a dropping funnel, and a reflux condenser, and then $poly(C'_3-$

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Table I MFI of PP-poly(C'_3 - C'_4) Composites

No.	S-1	S-2	S-3
Content of poly(GMA–DVB) (%) MFI (g/10 min)	$\begin{array}{c} 31 \\ 0.7 \end{array}$	$\begin{array}{c} 21 \\ 1.2 \end{array}$	$13 \\ 1.5$

 C'_4) (50 g) was dissolved into *n*-hexane at 70–80°C. Subsequently, a mixture of GMA (50 g)–DVB (10 g)– 2,2' azobisisobutylonitrile (2.2 g) was added dropwise. The polymerization was carried out for 2–3 h under N₂ atmosphere. After cooling, the product was recovered by putting the resultant solution into excess methanol and air dried. The monomer conversion was about 90%, which was determined by weighing the product.

Blending

Definite amounts of the resultant $poly(C'_3-C'_4)$ composites were mixed with the PP powder by using a mixer and then extruded at 230°C to prepare pellets by using an extruder with twin screws, with the poly(GMA–DVB) content adjusted to be 31%. Then, the resultant composite and PP were extruded to adjust the poly(GMA– DVB) content to be 21 or 13%. MFI of the pellets are shown in Table I.

Preparation of Microporous PP Fibers

Microporous PP fibers were prepared by spinning through a spinneret (diameter, 0.1 mm) at 270°C and successively stretched at 120°C.

Mechanical Properties

Tensile strength at yield, Young's modulus, and elongation to break were measured at 20 \pm 1°C



Figure 1 Relations between fiber finess and stretching ratio.

Table IIStretching Effect to Crystallinity ofMicroporous PP Fibers

Stretching Ratio	4	6	8	10
Crystallinity (%)	56.0	54.2	45.6	43.3

Estimated by X-ray diffraction. Sample S-3.

with the aid of a tensile tester, a Shimazu Autograph 200 from the Shimazu Corp., when the stretching rate and the distance between the chucks were 300%/min and 100 mm, respectively. The data shown were the average value of three samples (deviation, $\pm 5\%$).

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, a Poresizer 9310 from the Shimazu Corp.

Scanning Electron Microscopy

The texture of microporous PP fibers was observed by using 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 carried out by using Au ion sputtering for 3 min at 1.2 kV and 8-10 mA.

RESULTS AND DISCUSSION

Copolymerization of GMA and DVB

Copolymerization of GMA and DVB was carried out in a *n*-hexane solution of $poly(C'_3-C'_4)$. As the copolymerization proceeded, the effective stirring became difficult, although the stirrer itself rotated. Here, GMA and DVB are soluble in *n*hexane but not in poly(GMA). Then, the propagating poly(GMA) radicals phase separates; DVB also promotes the phase separation by crosslinking. Furthermore, the presence of $poly(C'_3-C'_4)$ makes the reaction system viscous, so the diffusion of the monomers to the propagating points is suppressed. Accordingly, the resultant copolymer becomes fine particles, which are dispersed in the $poly(C'_3-C'_4)$ phase, so it is easily blendable with PP.



Figure 2 Scanning electron micrographs of microporous PP fibers: surface and cross-section parallel to fiber axis.



Figure 3 Effect of stretching ratio to pore size, porosity, and specific surface area.

Preparation of Microporous PP Fibers

Both spinnability and stretchability of the PP composites were excellent, and whitening of the fibers by stretching was clearly observed, which means formation of a microporous structure. The PP phase is detouched and/or split at the periphery of poly(GMA–DVB) particles by stretching at the early stage, and further stretching causes formation of the microporous structure, as reported elsewhere.⁴

Figure 1 shows changes of the fiber fineness by stretching.

Reasonably, the larger the stretching ratio, the fiber denier decreases. Also, the larger the poly-

(GMA–DVB) particle content, the thicker the fiber. This suggests that poly(GMA–DVB) particles play a role as spacers among the split PP texture, as reported elsewhere.⁴

Table II shows a stretching effect to crystallinity of microporous PP fibers. The crystallinity decreases with increasing the stretching ratio. This tendency is similar to that of an ordinary PP fiber in the range of a stretching ratio of less than 10^5 .

Scanning Electron Microscopy

Figure 2 shows scanning electron micrographs of surfaces and cross-sections of microporous PP fi-



Figure 4 Effect of stretching ratio to tensile strength, Young's modulus, and elongation.

bers. On the surface, there are eliptical micropores parallel to the fiber axis. The cross-sections show a fibrous texture of PP parallel to the fiber axis, in which the minute particles of poly(GMA– DVB) are dispersed. However, some aggregated particles produced at the polymerization process can be observed, so it should be improved in the future. Also, it seems that the larger the particle content, the finer the fibrous texture.

Microporous Structure

Figure 3 shows the stretching effect on specific surface area, porosity, and average pore size of the fibers. They increase with increasing the stretching ratio and the poly(GMA–DVB) content. It is very interesting that the pore sizes are very minute and the specific surface areas are larger than 100 m²/g when the stretching ratio is 10.

Mechanical Properties

Figure 4 shows the stretching effect on tensile strength, Young's modulus, and elongation of microporous PP fibers. Evidently, with increasing the stretching ratio, tensile strength and Young's modulus increase and, contrarily, elongation decreases. These tendencies are consistent with those of ordinary PP fibers,^{5,6} but a little different from those in the cases of microporous PP fibers containing CaCO₃ or poly(methylsilsesquioxane) fillers,^{1,2} in which the stretching effect to tensile strength, Young's modulus, and elongation are relatively less. This might be attributed to the difference of the filler particle sizes and the filler contents. The details should be investigated further.

The values of tensile strength and Young's modulus are in almost same range as those of

ordinary PP fibers, and the values of elongation were smaller than those of ordinary PP fibers.⁵ It can be said that the microporous PP fibers have suitable mechanical properties to be used practically. These microporous PP fibers might be applicable to prepare cloth and nonwoven cloth as filters or separators.

CONCLUSION

GMA and DVB were copolymerized in an *n*-hexane solution of $poly(C'_3-C'_4)$, and the resultant composite was blended with PP. These PP composites were melt spun and stretched. The microporous PP fibers were thus prepared. Their porous structure are as follows: pore size, 0.01–0.03 μ m; porosity, 5–45%; and specific surface area, 10–180 m²/g, depending on the poly(GMA–DVB) particle content and stretching ratio. The mechanical properties are similar to ordinary PP fibers. However, the dispersion state of the poly(GMA–DVB) particles should be improved further.

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