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

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ABSTRACT: Styrene-divinylbenzene or glycidylmethacrylate-divinyl-benzene were copolymerized in powdery polypropylene suspended in water and the resultant polymer composites were blended with a definite amount of polypropylene. The products consisted of polypropylene and the fine particles of the copolymer, which were uniformly dispersed in polypropylene phase. These products were melt-spun to prepare polypropylene fibers containing the fine particles and then the fibers were stretched to make the fibers microporous. Some properties were estimated: porosity, 1.6-19.7%; average pore size, 0.004–0.009 µm; and specific surface, 9–137 m²/g. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 722-727, 1999

Key words: polypropyrene; styrene-divinylbenzene; glycidylmethacrylate-divinylbenzene; phase-separating copolymerization; microporous polypropylene fiber

INTRODUCTION

We reported that microporous polypropylene (PP) fibers were prepared by stretching PP fibers containing filler particles such as poly(methylsilsesquioxane) or CaCO₃.^{1,2} Here, the PP phase is split by stretching at the periphery of the filler particles and the resultant voids were widened by further stretching; the size of filler particles is one of the most important factors regarding the pore formation. Namely, the smaller the filler particles, the smaller the pore size. However, there is an inevitable limitation. It is the well-known tendency that the filler particles tend to aggregate much more with decreasing the particle size in nature. When very small filler particles are used, the pore size distribution of the resultant microporous PP fiber becomes relatively wider owing to aggregated particles. Accordingly, the key point is

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Journal of Applied Polymer Science, Vol. 74, 722-727 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/030722-06 how to make very fine particles uniformly dispersed in the PP phase with no aggregation. On the other hand, we reported that copolymerization of styrene (St)-divinylbenzene (DVB) in polyvinylchloride gel phase results in the polymer composite, in which very small particles of poly(St-DVB) were uniformly dispersed in the polyvinylchloride phase.^{3–5}

Therefore, we copolymerized St-DVB or glycidvlmethacrvlate (GMA)-DVB in powderv PP suspended in water. Then, the resultant PP composites were blended with PP and then melt spun to prepare PP fibers containing very fine particles of poly(St-DVB) or poly(GMA-DVB), which were successively stretched to make the fibers microporous.

EXPERIMENTAL

Materials

PPs used were PN-540 [melt flow index (MFI) at 230°C (MFI), 8.0 g/10 min; mp, 135°C] and PN-

Table I Recipes and Polymerization Results^a

No.	St-DVB (g)	BPO (g)	Poly(St-DVB) (g)	Monomer Conversion (%)
Z-1	20	0.8	18	90
Z-2	30	1.2	28	93
Z-3	40	1.6	39	98
Z-4	50	2.0	49	98

 $^{\rm a}$ DVB/St = 1/10 by weight; (St + DVB)/BPO = 56.9 by molar ratio.

120 (MFI, 1.8 g/10 min; mp, 158°C) from Tokuyama Corp. St, GMA, DVB, benzoylperoxide (BPO), and 2,6-di-t-butyl-4-methylphenol (antioxidant) were of commercial grade. The purity of DVB was 55%. All the monomers were pretreated with silica gel to exclude inhibitor.

Copolymerization

Water (800 mL) and powdery PN-540 (200 g) were put into a separable flask (1 L) attached with a stirrer, a reflux condenser, and a dropping funnel. Definite amounts of the St-DVB or GMA-DVB mixture was added dropwise with stirring under nitrogen atmosphere. Reaction temperature was controlled to be 90 \pm 5°C and the copolymerization was carried out for 4 h. Then, the reaction products were recovered by filtration, rinsed with methanol, and air dried. The monomer conversion was calculated from the weight change by the copolymerization.

The recipes are shown in Tables I and II.

Blending

Definite amounts of the copolymerization product, PN-120, and the antioxidant (1.3%) of total



Z-2



Z-6

Figure 1 Transmission electron micrographs of the PP composites containing poly(St-DVB) and poly(GMA-DVB) particles.

amount of PN-540 and PN-120) were well mixed in advance and then blended at 230–250°C to prepare pellets by using an extruder with twin screws.

Spinning and Stretching

The polymer blends were extruded to melt-spin the fibers at 270°C (draft ratio, 7–10) and succes-

GM No.	IA-DVB BI (g) (g	PO (GMA- g) Mol	DVB)/BPO Poly(G ar Ratio	Mono MA-DVB) Conve (g) (%	omer ersion
Z-5	20 0	.6	54	11 55	5
Z-6	25 1	.0	42	17 68	8
$ m Z\text{-}7^{b}$	30 0	.9	54	14 47	7
Z-8	30 1	.2	42	22 73	3
Z-9	35 1	.4	42	27 77	7
Z-10	40 1	.6	42	34 85	5

Table II Recipes and Polymerization Results^a

^a DVB/GMA = 1/10 by weight.

 $^{\rm b}$ Polymerized with no N_z substitution.

No.	PN-120 (g)	PN-540 (g)	Poly(St-DVB) (g)	Poly(St-DVB)/Total Polymer (%)	MFI (g/10 min)
Z-1	400	200	18	2.9	3.0
Z-2	400	200	28	4.4	2.8
Z-3	400	200	39	6.1	2.3
Z-4	400	200	49	7.6	2.2

Table III Blending

sively stretched at 120° C (stretching ratio, 10 or 12).

Mechanical Properties

Tensile strength at yield (TS), Young's modulus (YM), and elongation to break (Eb) were measured at $20 \pm 1^{\circ}$ C by using 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 fibers were measured by using an Hg porosimeter, Poresizer 9310 from Shimazu Corp.

Transmission Electron Microscopy

The test piece was embedded in an epoxy resin and then treated with RuO_4 for 4 h after trimming. The ultrathin sample was prepared by using an ultra-microtome, a Reichert-Nissei UL-TRACUT-N from Leica AG. The transmission electron microscope used was JEM 200CX from JEOL Ltd.

Scanning Electron Microscopy

The fibrous texture of the microporous PP fibers was observed with the aid of a scanning electron

49	7.6	2.2	
10 or	microscope, JSM-220 from JEOL Ltd.	The accel-	

erated 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

Copolymerization

First, the St-DVB-BPO or GMA-DVB-BPO mixture is soaked into PP phase and then the radical copolymerization is initiated. Propagating polystyryl or polyglycidylmethacryl radicals are incompatible with the PP phase and phase-separate out. Furthermore, DVB promotes the phase separation. Also, the migrating rate of the monomers to the polymerizing points should be so small in the very viscous PP phase that the resultant cross-linked copolymers become fine particles uniformly dispersed with no aggregation, as shown in Figure 1.

Tables I and II show the results of the copolymerizations.

In the case of the St-DVB system, the monomer conversions were larger than 90% and the monomer conversion increases with increasing the weight ratio of (St-DVB)/PP. In the case of the GMA-DVB system, the monomer conversion increases with increasing the weight ratio of (GMA-

No.	PN-120 (g)	PN-540 (g)	Poly(GMA-DVB) (g)	Poly(GMA-DVB)/Total Polymer (%)	MFI (g/10 min)
Z-57	400	400	25	3.0	4.9
Z-6	200	200	17	4.1	2.9
Z-8	200	200	22	5.2	3.2
Z-9	200	200	27	6.3	3.1
Z-10	200	200	34	7.8	3.3

Table IV Blending^a

 $^{\rm a}$ Z-57: Z-5 and Z-7 were blended together with PN-120.



Figure 2 TS, YM, and Eb vs poly(St-DVB) or poly(GMA-DVB) content. The fiber finenesses of poly(St-DVB) and poly(GMA-DVB) systems were 50–70 and 60–80 denier, respectively.

DVB)/PP and the conversions are smaller in comparison with those in the case of St-DVB system. This is explicable by the less affinity of GMA-DVB for PP than St-DVB.

Since the radical copolymerizations were carried out in the PP phase, some interaction should occur between the PP molecules and the propagating polymer radicals, although the details are obscure.

Preparation of Microporous PP Fibers

The melt-spun fibers containing the fine particles of poly(St-DVB) or poly(GMA-DVB) system are stretched. There were no problems regarding melt spinning and stretching. The PP phase is split at the periphery of the copolymer particles at the earlier stage of stretching and the resultant minute voids are enlarged by further stretching.

The microporous fibers are prepared.

Blending

Tables III and IV shows the blending recipes and results. The blending was carried out with no problem in all the cases.

Mechanical Properties

Figure 2 shows dependencies of TS, YM, and Eb onto the poly(St-DVB) and poly(GMA-DVB) contents. In both the cases of poly(St-DVB) and poly(GMA-DVB) systems, TS, YM, and Eb similarly increase with increasing the poly(St-DVB)



Figure 3 Porosity, pore size, and specific surface area vs poly(St-DVB) or poly(GMA-DVB) content.



Surface



Cross-section

Figure 4 Scanning electron micrographs of microporous PP fiber (Z-2).

and poly(GMA-DVB) contents, respectively. Also, these values show that these microporous PP fibers are practically applicable. The TS, YM, and Eb values of the poly(St-DVB) system are not so different from those of the poly(GMA-DVB) system. However, these differences presumably come from the differences in the sizes of the polymer particles and their dispersion states, and the details should be studied further.

Microporous Structure

Figure 3 shows dependencies of porosity, pore size, and specific surface area onto the poly(St-DVB) and poly(GMA-DVB) contents. Porosity, pore size, and specific surface area increase with increasing the poly(St-DVB) and poly(GMA-DVB) contents in both cases of poly(St-DVB) and poly(GMA-DVB) systems, respectively. It is interesting that the pore sizes are very minute due to very small sizes of poly(St-DVB) and poly(GMA-DVB). Also, specific surface areas are large, con-

sidering porosity values. The porosity and specific surface area values of the poly(St-DVB) system are larger than those of the poly(GMA-DVB) system and the pore size values of the poly(St-DVB) system are rather similar to those of the poly(GMA-DVB). These situations are inexplicable now and should be studied further. It is elucidated that the microporous structures are very fine in both the cases.

Scanning Electron Microscopy

Figures 4 and 5 show scanning electron micrographs of microporous PP fibers (Z-2 and Z-6) of St-DVB and GMA-DVB systems, respectively. Stripe patterns and fibrous textures, parallel to the fiber axes, are observed in both the surfaces and the cross sections, respectively. These structures result from splitting of the PP phase by stretching. It is interesting that the fine particles are scarcely observed in the fibrous textures, showing that they are very minute.



Surface



Cross-section

Figure 5 Scanning electron micrographs of microporous PP fiber (Z-6).

Since the radical copolymerizations of the monomers were carried out in the PP phase, some interaction should occur between the PP molecules and the resultant copolymer particles. Also, it presumably affects the properties of the microporous PP fibers: mechanical properties and porous structure. However, the details should be studied further.

CONCLUSION

Microporous PP fibers are prepared by using the PP composites containing very fine particles of poly(St-DVB) or poly(GMA-DVB), which prepared by copolymerization of St-DVB or GMA-DVB in PP powder suspended in water.

The PP composites were extruded to melt spin the fibers, which were successively stretched to make the fibers microporous. Namely, the PP phase is split at the periphery of the copolymer particles to result in microvoids at the early stage of the stretching, which were enlarged by further stretching. These microporous PP fibers have mechanical properties enough to be used practically. Also, their microporous structures are very fine, as shown below.

Poly(St-DVB) system: porosity, 5–20%; pore size, $0.01 > \mu m$; and specific surface area, $50-150 m^2/g$.

Poly(GMA-DVB) system: porosity, 2–12%; pore size, $0.01 > \mu m$; and specific surface area, 9–116 m²/g.

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