

NOTE

Dyeable Polypropylene Fiber

INTRODUCTION

Many investigations have been carried out to make polypropylene (PP) fiber dyeable. For example, it was reported that blending of poly(glycidylmethacrylate-*co*-styrene) or poly(glycidyl methacrylate-*co*-vinyltoluene) was effective to improve the dyeability of the resultant fibers.¹ We also reported that a polymeric fine powder of glycidyl methacrylate (GMA)-divinylbenzene (DVB) (particle size, 0.1 μm) is useful as a mordant.² It was elucidated that the introduction of an epoxy group into PP fibers is effective to make the fiber dyeable and to endow color fastness for washing.

However, it is not so easy to blend the bulky polymeric fine powder with PP. Furthermore, the color of the dyed fiber was rather dull. The polymeric fine powder was prepared by copolymerizing GMA-DVB in cyclohexane, a poor solvent for poly(GMA).³ In this article, we report the copolymerization of GMA-DVB in molten PP instead of cyclohexane with the aid of an extruder, and the resultant PP composite was melt-spun to prepare a PP fiber and its dyeability was investigated.

EXPERIMENTAL

Materials

The PP powder was the product of the Tokuyama Corp. (MFI, 16). GMA, DVB, and di-*t*-butylperoxide (an initiator of radical polymerization) were of commercial grade. The carrier and the surface-active agent used for dyeing were 1-methylnaphthalene and a nonionic liquid detergent, Humming, from Kao Co., respectively. Dyestuffs used were as follows: Sumikaron Turquoise Blue S-GL, Sumikaron Red E-FBL, Sumikaron Brilliant Red SE-BL, Sumikaron Blue E-FBL, and Sumikaron Orange SE-B from Sumitomo Chemical Co. and Kayalon Polyester Yellow YL-SE, Kayalon Polyester Red BL-E, and

Kayalon Polyester Blue EBL-E from Nippon Oil & Fats Co.

Preparation of PP Composite

The PP powder was well mixed with a mixture of GMA-DVB di-*t*-butylperoxide [DVB/(GMA + DVB) = 0.05 by wt, di-*t*-butylperoxide/(GMA + DVB) = 0.01 by wt, and (GMA + DVB)/PP = 0.07 by wt]. Then, the mixture was extruded at 170–200°C with the aid of an extruder with twin screws. The resultant pellet was kept at 70°C under reduced N₂ atmosphere overnight.

Spinning

The PP fiber was spun at 200–290°C by extruding the PP composite pellets with 2,6-di-*t*-butyl-4-methylphenol (antioxidant, 0.6% of PP by wt) through a die with 198 spinnerets (diameter, 0.7 mm) and then stretched at 150°C. The draft and stretching ratios were 170 and 6, respectively.

Transmission Electron Microscopy

The fiber was embedded in an epoxy resin and then treated with RuO₄ for 48 h after trimming. The ultrathin sample was prepared by using an ultramicrotome, a Reichert-Nissei ULTRACUT-N from Leica AG. The transmission electron microscope used was a Hitachi H-8000 from Hitachi Ltd.

Mechanical Properties of PP Fiber

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

Dyeing

The carrier (4 g) and a small amount of the surface-active agent were added into water (1 : L) and the



Figure 1 Transmission electron micrograph of cross section of the PP fiber.

pH of the solution was adjusted by adding anhydrous sodium acetate (1 g) and acetic acid (0.25 g). Then, a dyestuff (0.2 g) and PP fiber (1 g) were successively added into the solution (50 mL). The dyeing was carried out at the boiling point for 1 h. The dyed fiber was rinsed well with a hot aqueous solution containing a small amount of the detergent and subsequently with water. Furthermore, the dyed fiber was rinsed with acetone by using a Soxhlet extractor until no color elusion could be detected.

RESULTS AND DISCUSSION

The PP composite was prepared by copolymerizing GMA-DVB in molten PP with the aid of the extruder. GMA and DVB are compatible with molten PP, while the propagating poly(GMA) radicals are incompatible with it and separate out of the molten PP phase. Furthermore, DVB promotes the phase separation, and diffusion of the monomers in the very viscous molten PP should be very slow. Consequently, the resultant poly(GMA-DVB) is very finely and uniformly dispersed in the PP phase. Since the copolymerization is of a radical mechanism, the propagating polymer radicals should interact with the PP molecules. Therefore, it might be presumed that some graft polymers could be formed between poly(GMA-DVB) and PP and it suggests formation of a gel. The PP composite was extracted with *m*-xylene using a Soxhlet extractor in order to estimate the amount of the gel fraction. It is very interesting that no residue was detected in a cylindrical filter paper, suggesting that pure poly(GMA-DVB) and the graft polymer are very minute. This is very important in relation to the excellent spinability of the PP composite. Figure 1 shows a transmission electron micrograph of the fiber cross section, supporting the discussion described above. The diameter of the minute poly(GMA-DVB) is of 10 nm order.

Fiber Properties

Table I shows some fiber properties. The values of the tensile strength, Young's modulus, and elongation show the practical applicability of the PP fiber in comparison with the values of the PP fibers.^{4,5} Crystallinity of the fiber is similar to that of the PP fibers.⁴ However, the epoxy value is pretty small in comparison with that calculated from the recipe, as-

Table I Fiber Properties

Fiber	Fineness (d) ^a	Crystallinity ^b (%)	Epoxy Value ^c (mmol/g)	Tensile Strength (g/d)	Young's Modulus (g/d)	Elongation (%)
Dyeable PP fiber	2.6	55	0.1	7	64	23
Unmodified PP fiber ^d	1.9	55	—	8	70	20

^a Denier.

^b Determined with the aid of an X-ray spectrometer, RU-200E from Rigaku Denki Corp., rotating the sample disk (92 rpm).

^c Calculated from oxygen content by elementary analysis.⁶

^d Draft and stretching ratios, 170 and 5, respectively.

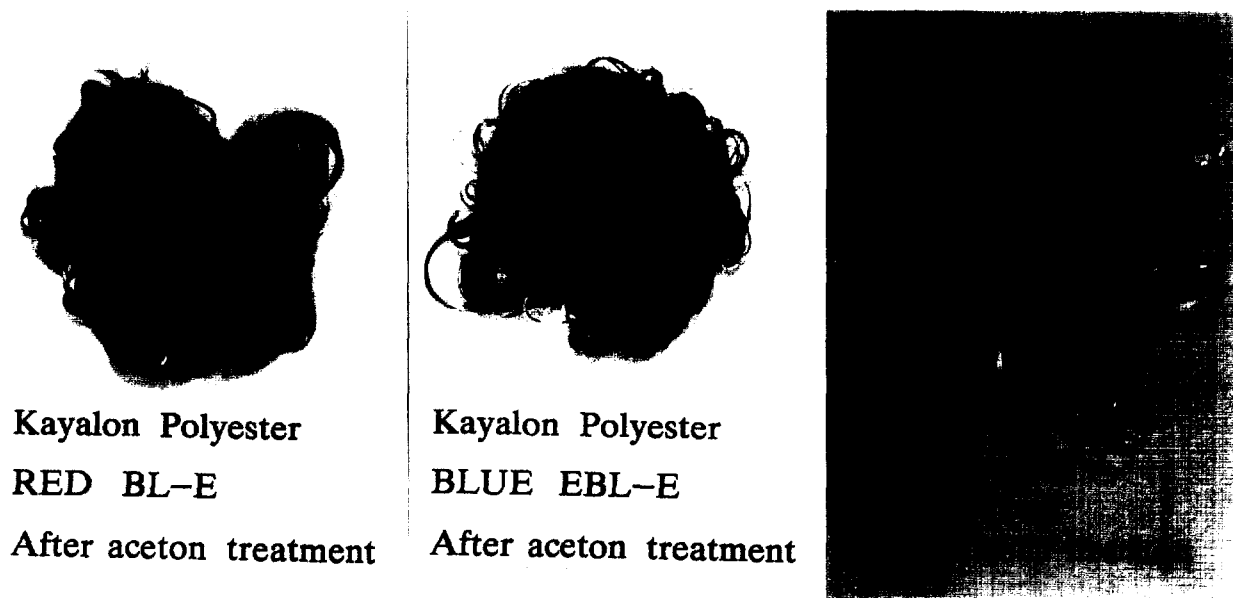


Figure 2 Some samples of dyed fibers.

suming that the monomer conversion was 100%. This suggests that the details of the copolymerization should be studied further.

Dyeability

The PP fiber could be well dyed with all the dispersion dyestuffs by carrier dyeing, although the epoxy value of the fiber was pretty small against expectation. If the dyestuffs have functional groups such as amino and/or phenolic hydroxy groups, which are reactive with the epoxy groups, the dye molecules could be anchored onto the poly(GMA-DVB) component. The chemical structure of the dyestuffs used are not evident, but no discoloration of the dyed fibers was observed by the treatment with acetone. It evidently supports that the dye molecules are fixed onto the finely dispersed poly(GMA-DVB) component by chemical bonding. Furthermore, it is interesting that the dyed fibers have a luster. Figure 2 supports this result. However, the details about the dyeing conditions and the relation between the color shade and the epoxy value of the fiber should be studied further.

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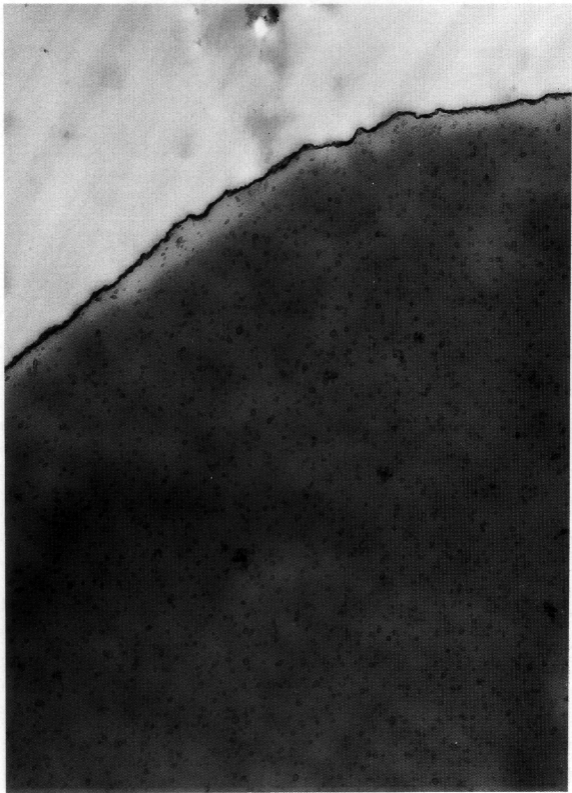


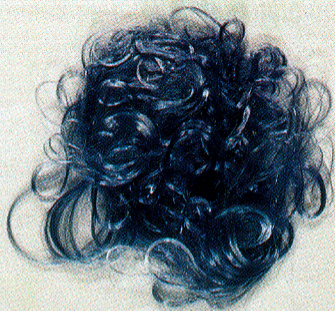
Figure 1 Transmission electron micrograph of cross section of the PP fiber.



Kayalon Polyester

RED BL-E

After acetone treatment



Kayalon Polyester

BLUE EBL-E

After acetone treatment



Sumikaron

OrangeSE-B

After acetone treatment

Figure 2 Some samples of dyed fibers.