Dyes and Pigments, Vol. 35, No. 4, pp. 367–373, 1997

PII: S0143-7208(96)00109-X 0143-7208/97 $17.00+0.00

Inducing Water Bath Dyeability in Polypropylenic Fibers by their Blending with Polyamide 6

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(Received 5 September 1996; accepted 7 October 1996)

ABSTRACT

Melted blends of polypropylene and polyamide 6 compatibilized with a poly(propylene)/maleic anhydride copolymer were extruded and stretched to give filaments. The polypropylenic fibers obtained by this method were found to be easily dyeable in an aqueous dyebath. The wet-washing at 40, 60, and 90°C and the light and dry-cleaning fastnesses of the new material appeared quite satisfactory. © 1997 Elsevier Science Ltd

INTRODUCTION

The use of conventional direct dyeing techniques for colouring polypropylene fibers is limited by their lack of dyeability. In fact, their lack of dyeability together with their stiffness are the main disadvantages in their use. On the other hand, these fibers have a wide range of applications due to their high strength, resistance, and lightness.

In previous work [1], in order to prepare dyeable polypropylenic fibers, we suggested blending isotactic polypropylene with hydrogenated oligocyclopentadiene, two polymers miscible in the melt. The resulting fibers, dyed in an aqueous dyebath, showed better light, wet-washing and dry-cleaning fastness properties than pure polypropylene, while retaining similar static mechanical properties.

In this work, we present another method for the production of polypropylenic fibers dyeable in an aqueous dyebath, consisting in melt mixing polypropylene with polyamide 6. As these polymers give strongly incompatible blends, the use of an appropriate interfacial agent is needed in order to obtain a good adhesion and a homogeneous dispersion of the polyamide particles in the polypropylene matrix [2–4]. Compatibilization is a valid solution for recycling degraded polymeric materials. In fact, melted blends of polypropylene, polyamide 6 and compatibilizing agent can be extruded and stretched to give filaments of an essentially new material with a wide range of textile properties. Furthermore, the above compatibilized blends can be used to prepare films or sheets characterized by enhanced mechanical properties.

Some results of this work have been recently given [5].

EXPERIMENTAL

Binary blends of isotactic propylene/ethylene random copolymer containing 6% ethylene (Daplen KFC 2206), manufactured by Petrochemie Danubia, (PP), and polycaprolactam (Grilon F34), manufactured by EMS Chemie, (PA6), were prepared by melt mixing in a double screw extruder.

The compatibilized blend of PP and PA6 in a weight ratio 70/30 was prepared by adding, to 100 parts of the binary blend, 2.5 parts of a polypropylene modified with 1% of grafted maleic anhydride (Orevac CA100), manufactured by ELF Atochem, (OR), as the compatibilizing agent.

The blends were extruded in form of filaments in a microextruder at 260°C. Spun filaments were drawn with a ratio 1:3.5.

Optical microscopy (OM)

The filaments were microtoned in a perpendicular direction to the fiber axis. The cross section of the fiber was examined with a Wild microscope.

Scanning electron microscopy (SEM)

The samples, fractured under liquid nitrogen, were observed with a scanning electron microscope (Philips model 515) operated at 9.3 kV. The surfaces of the fractured specimens were coated with gold.

Differential scanning calorimetry (DSC)

A Perkin Elmer DSC-4 thermal analysis data station system was used. The samples (about 4 mg) were heated from –40°C to 270°C at a scanning rate of 10°C min^{-1} and then cooled down to –40°C at the same scanning rate.

Mechanical tensile tests (MA)

Stress–strain curves were obtained using an Instron tensile tester at 65% R.H. and 20°C, at a cross-head speed of 200 mm min^{-1}. The gauge length was

25 cm. Young's moduli, stress and elongation at break were calculated from stress–strain curves as an average of 20 specimens.

Dynamic mechanical thermal analysis (DMTA)

Measurements were carried out with a dynamic mechanical thermal analyzer (Polymer Laboratories, Ltd) MK III with the sample presented in the tensile mode at a frequency of 1 Hz and a strain ×1. Polymer specimens in the form of filaments were investigated in the temperature range from –20°C to 120°C with a heating rate of 3°C min^{-1}.

Dyeing procedure

For the dyeing experiments, an AHIBA apparatus was used. The fibrous materials were first washed at 60°C in water containing 0.25% of tenside, then washed with water and dried. Dyeing was carried out in water (bath ratio 1:40) with 1% (w/w) of dyestuff starting at 40°C, then raising the temperature to 98°C over 45 min and maintaining this temperature for 1 h. The following commercial disperse dyes were used: C.I. Disperse Red 13 (monoazo) and C.I. Disperse Blue 3 (anthraquinone), usually employed for poly(ethylene terephthalate) (PET) fibers. The exhaustion of each sample bath and the corresponding dye uptake were estimated from the calibration curves by spectrophotometric measurements.

The quantitative evaluation of the colour intensity of the fibrous materials was carried out using reflectance data obtained by an Elrepho Zeiss photometer.

Colour fastnesses to artificial light, wet-washing and dry-cleaning

The determination of colour fastness to artificial light (xenon arc lamp) was performed using a Xenotest Hanau 150 S (Heraeus); assessments were carried out according to UNI 7639 (ISO 105-B02).

Wet-washing and dry-cleaning fastness tests were carried out according to UNI 7638 (ISO 105-C01/03/04) and UNI 8268 (ISO 105-D01), respectively; petroleum spirit was used as the solvent.

RESULTS AND DISCUSSION

Blending of incompatible polymers gives materials having poor interfacial adhesion and dispersion and poor mechanical properties with respect to the parent compounds. On the other hand, polymer blending can give a positive answer to the ever growing industrial demand for new materials with a low cost/price ratio.

Several efforts have been devoted to compatibilize blends of polyolefins and polyamides; in particular, functionalized polyolefins, able to react with the terminal amino groups of polyamide, have been found to be effective as interfacial agents [2]. It has been recently [2–4] reported that the presence of compatibilizer OR leads to a significant lowering of the surface tension of PA6. In particular, it has been observed that the polarity of PA6 is partially cancelled in the blend by the reaction of the maleic anhydride moiety of OR with the terminal amino groups of PA6.

In this work, fibers obtained from PP/PA6 blends compatibilized with OR have been considered. The composition of the polymer system was PP/PA6/OR 70/30/2.5 by weight.

The DSC scans of the fibers showed two endothermic peaks of melting as they were heated up to 260°C, and two exothermic peaks of crystallization when cooled from the melt, in both cases the two signals being related to PP and PA6 structures, respectively. The degrees of crystallinity were calculated from the melting enthalpies ($\alpha_{cr,m}$) and from the crystallization enthalpies ($\alpha_{cr,cr}$) assuming melting enthalpy values for 100% crystalline PP and for 100% crystalline PA6 of 44 cal g^{-1} and 55 cal g^{-1}, respectively [6] (Table 1). According to the reported [2] results obtained for the compatibilized isotropic (not drawn) 70/30/2.5 PP/PA6/OR blend, the degree of crystallinity $\alpha_{cr,crPA6}$ has been found to decrease in the presence of the compatibilizing agent with respect to the plain blend.

The SEM micrographs of cross and longitudinal sections of the 70/30/2.5 PP/PA6/OR filaments are collected in Fig. 1: no microdomains of PP are observed, suggesting a higher compatibilization between the components of the blend.

The tensile testing results, obtained considering 70/30/2.5 PP/PA6/OR and PP filaments (Table 2), show similar values of Young's modulus and tenacity of the two samples. For the same systems, typical curves of log E′ *vs.* temperature from DMTA measurements are reported in Fig. 2. It can be observed that the storage moduli of PP are higher than those of the compatibilized

TABLE 1
Thermal Behavior of Plain and Compatibilized 70/30 PP/PA6 Filaments

Filament	α_{PP} *(cr,m)*	α_{PA6} *(cr,m)*	α_{PP} *(cr,cr)*	α_{PA6} *(cr,cr)*	$T_{m(PP)}$ *(°C)*	$T_{m(PA6)}$ *(°C)*	$T_{c(PP)}$ *(°C)*	$T_{c(PA6)}$ *(°C)*
PP/PA6 70/30	19.6	7.8	20.2	10.5	151	224	104	185
PP/PA6/OR 70/30/2.5	21.2	10.5	23.2	5.6	150	220	103	179

Fig. 1. SEM micrographs of cross and longitudinal sections of 70/30/2.5 PP/PA6/OR filaments.

blend; however, the trends are similar in the two cases, thus evidencing a high dispersion of PA6 in PP.

The dye uptake of C.I. Disperse Red 13 and of C.I. Disperse Blue 3 appeared quite satisfactory and the cross-section of dyed filaments, observed with an optical microscope, evidenced in every case a uniform distribution of the dye. The reflectances of samples dyed with C.I. Disperse Red 13 and C.I. Disperse Blue 3, washed in water and dried, were respectively 13% and 51%, taking up to 100% the reflectance of undyed filaments.

The wet-washing fastnesses at 40, 60 and 90°C, as well as the light and dry-cleaning fastnesses of compatibilized fibrous materials, were found to be similar to, or higher than, those of the industrial PET and of the previously blended PP[1], chosen as references (Table 3).

TABLE 2

Tensile Mechanical Properties of 70/30/2.5 PP/PA6/OR and PP Filaments at 20°C and at 65% R.H.

Property	*PP/PA6/OR 70/30/2.5*	*PP*
Titre (den)	254	
Diameter (μm)	150	
Young's modulus (g den^{-1})	19.6	20–25
Stress at maximum (g)	605	
Strain at break (%)	17.9	
Tenacity at maximum (g den^{-1})	2.4	2.5–3.0
Stress at break (g)	221	
Shrinkage at 100°C (%)	2.5	2.5

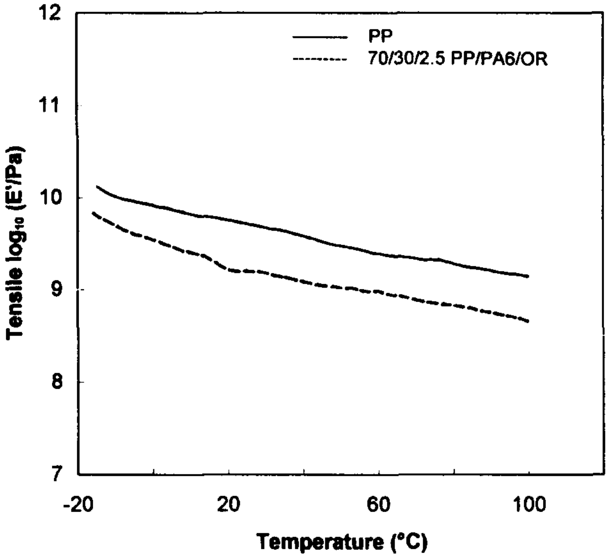

Fig. 2. DMTA measurements of pure and blended PP.

TABLE 3

Colour Fastness to Artificial Light, Wet-washing and Dry-cleaning of Industrial PET, previously blended PP[a] and PP/PA6/OR Yarns

Yarn	*PET*		*PP/HOCP 85/15*		*PP/PA6/OR 70/30/2.5*	
Dye	*C.I. Disperse*		*C.I. Disperse*		*C.I. Disperse*	
	Red 13	*Blue 3*	*Red 13*	*Blue 3*	*Red 13*	*Blue 3*
Light	4	4–5	4	5	4	6
Wet-washing (40°C)	5	5	5	5	5	5
Wet-washing (60°C)	4	4–5	4	4–5	4–5	5
Wet-washing (90°C)	4–5	4	1–2	1–2	4–5	4
Dry-cleaning[b]	—	—	4	3–4	5	5

[a]Ref. 1; [b]Petroleum spirit.

CONCLUSION

Industrial fibers obtained by blending PP with PA6 have good spinability and mechanical properties. The dyeing experiments showed that the uptake of the dye from the dyebath is excellent. The affinity of disperse dyes for the disperse fraction of PA6 increases the dyeability of the new fibrous materials. Light, wet-washing (at 40, 60, and 90°C) and dry-cleaning fastnesses of the new fibers are comparable to those of PET fibers.

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