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Blending Polypropylene with Hydrogenated Oligocyclopentadiene: A New Method for the Production of Dyeable Fibers

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ABSTRACT

Conventional direct dyeing techniques have limited use for the coloration of polypropylene fibers. In this paper, blends of isotactic polypropylene (iPP) with hydrogenated oligocyclopentadiene (HOCP), a glassy amorphous resin, have been used for the preparation of fibers dyeable in an aqueous dyebath. These fibers show better light, wet-washing and cleaning fastness properties than iPP while retaining similar statical mechanical properties.

INTRODUCTION

Polypropylene fiber has a wide range of applications; the fiber is characterized by high strength and lightness and by good resistance to abrasion

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and chemicals; the main disadvantages in its use are its stiffness and lack of dyeability.

Dyeing of isotactic polypropylene (iPP) fibers by conventional direct techniques (i.e. from an aqueous dyebath) is generally ineffective as a consequence of two main factors:

(1) insufficient chemical affinity between the fiber and dyestuff, due to the absence of ionic or polar groups on the polymer chain, so that the retention of dye molecules is due only to the presence of weak Van der Waals' forces.
(2) the poor accessibility of dyestuff on fibers, due to the high degree of crystallinity of iPP.

In order to make iPP fibers dyeable, many methods have been suggested.[1]

This present work demonstrates that blending iPP with hydrogenated oligocyclopentadiene (HOCP), a low molecular weight amorphous resin derived from hydrocarbons, makes it possible to obtain fibers dyeable using conventional direct dyeing techniques.[2]

The thermal and crystallization behavior of iPP/HOCP blends has been investigated in a previous study.[3] Each blend exhibited a single glass transition temperature (T_g) with a value which increased with increasing HOCP content.

Examination of isothermally crystallized samples by optical microscopy showed that the films were completely filled with spherulites, and no segregation of HOCP could be observed.

The spherulite growth rate and overall kinetic rate constants were lowered by dilution of iPP with HOCP. The equilibrium melting point decreased with HOCP concentration, and the Flory–Huggins interaction parameter was negative and close to zero. On the basis of these experimental data, it was concluded that iPP and HOCP were miscible in the melt and formed a homogeneous amorphous phase.

Wide- and small-angle X-ray scattering studies[4] showed that the apparent crystal size of iPP was not modified by the presence of HOCP and that the long period increased as a function of HOCP content, suggesting that HOCP was mainly distributed in the amorphous interlamellar regions.

Dynamic and static mechanical studies of iPP/HOCP blends[5,6] confirmed the miscibility of the two components in the amorphous regions; due to the high T_g of HOCP (67°C), the addition of HOCP results in an increase in the rigidity of the system.

Oxygen transport through membranes of iPP/HOCP blends has also been studied;[7] an increase of HOCP content causes the T_g of the blends to rise, and lowers oxygen permeability and diffusion through the films.

EXPERIMENTAL

Sample preparation

Binary blends of iPP (MOPLEN T30S, mol. wt 300 000, Montedison) and HOCP (ESCOREZ, mol. wt 630, Esso Chemical) were prepared by melt-mixing in an extruder at 240°C; blends with weight ratios of 100/0, 90/10 and 85/15 were obtained.

The blends were extruded in the form of filaments with a draw ratio of 1 : 2·5 by using the following conditions: extrusion temperature 230–250°C, quenching length 5 m, stretching speed 200 m min^{-1} and stretching hot rolls temperature 140°C. Yarns of 70 den and 30 filaments were obtained and used in the experiments; knitted fabrics, obtained by a circular knitter, were used in the dyeing experiments.

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 200°C at a scanning rate of 10°C min^{-1}.

The apparent enthalpies of fusion (ΔH) of the blends were calculated from the areas of the DSC endothermic peaks. The crystalline (α_{cr}) and amorphous (α_{am}) weight fractions were calculated from the following relations:

$$\alpha_{\text{cr}} = \Delta H/\Delta H_{\text{iPP}} \tag{1}$$

$$\alpha_{\text{am}} = (1 - \alpha_{\text{cr}}) \tag{2}$$

where ΔH_{iPP} (184 J g^{-1}) is the melting enthalpy of 100% crystalline iPP.[8]

Wide-angle X-ray scattering (WAXS)

WAXS profiles of fibers were obtained with a D 500-Siemens diffractometer (Cu Kα nickel-filtered radiation) in the reflection mode, scanning 2θ angle in continuous mode. The X-ray diffraction patterns were also obtained with the Siemens apparatus, by a transmission method, and recorded on film. The crystalline orientation was evaluated by measuring the intensity distribution of X-ray diffraction around the Debye rings. The apparent crystal size of iPP in the direction perpendicular to the 040 and 110 crystallographic planes was calculated from the breadth of the reflections.

Mechanical tensile tests

Stress–strain curves were obtained using an Instron tensile tester at 65% RH and 20°C, at a cross-head speed of 20 mm min^{-1}. Specimens consisted of yarns, and of yarns formed into one knot; the test carried out on the yarns formed into one knot was to evaluate the mechanical properties of the yarn in a direction perpendicular to the yarn axis. Young's modulus, stress and elongation at rupture were calculated from stress–strain curves as an average of 15 specimens.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical tests were made by using a Polymer Laboratories DMTA unit operated in the tensile mode. A heating rate of 3°C min^{-1} and a frequency of 1 Hz were used. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta = E''/E'$) were calculated as a function of temperature for each blend. The T_g was taken as the maximum of the $\tan \delta$ peak.

Birefringence

The birefringence (D*n*) of the fibers was determined with a polarizing light microscope equipped with a Leitz Berek compensator.

Dyeing procedure

For the dyeing experiments an AHIBA apparatus was used. The knitted fabrics 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% (omf) 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, usually employed for poly(ethylene terephthalate) (PET) fibres, were used: CI Disperse Red 13 (monoazo), CI Disperse Yellow 5 (diazo), CI Disperse Blue 3 (anthraquinone). 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 color intensity of the knitted fabrics was carried out using reflectance data obtained on an Elrepho Zeiss photometer.

Light, wet-washing and dry-cleaning fastness

Light fastness determination was performed using a Xenotest Hanau 150S (Heraeus); assessments were carried out according to UNI 7639 (ISO 105/V).

Wet-washing fastness tests were carried out according to UNI 7638 (ISO 105/IV) and dry-cleaning fastness according to UNI 8268 (ISO 105-DO1); petroleum spirit was used as the solvent.

RESULTS AND DISCUSSION

Table 1 gives the thermal properties and the birefringence values of iPP and iPP/HOCP blends.

As expected, the apparent calorimetric melting temperature (T_m) and α_{cr} decreased with increasing HOCP concentration in the yarn, i.e. α_{am} of blend yarn increased with increasing HOCP content of the blends.

Birefringence values of iPP and iPP/HOCP filaments were almost the same (Table 1); this indicates that the overall orientation of the crystalline and amorphous zones along the fiber axis are the same in both cases. The low birefringence values are the result of the low stretching ratio.

X-ray analysis reveals that the spacing values of iPP diffractions were constant for pure iPP and for the blends, and that the intensity of the crystalline diffractions of iPP decreased with increasing HOCP fraction of the blend.

The X-ray diffraction photographs of iPP and iPP/HOCP fibers show that, during the unidirectional deformation of the spinning process, the spherulitic morphological structure changed into a characteristic fibrillar structure, and that the orientation of the crystallites was not modified by the presence of HOCP.

TABLE 1

Thermal Properties and Birefringence Values of iPP and iPP/HOCP Yarns

Properties	*iPP*	*iPP/HOCP*	
		90/10	*85/15*
α_{cr}	0·58	0·52	0·5
α_{am}	0·42	0·48	0·5
T_g (°C)[a]	9	55	72
T_m (°C)	172·8	168·4	162·2
Δn	0·020	0·021	0·020

[a] From tan δ max.

TABLE 2
Mechanical Properties of iPP and iPP/HOCP Yarns

Mechanical parameter	*iPP*		*iPP/HOCP 90/10*		*iPP/HOCP 85/15*	
	Yarns	*One knot yarns*[a]	*Yarns*	*One knot yarns*[a]	*Yarns*	*One knot yarns*[a]
Stress to break (g)	268 ± 6·1	273 ± 12	272 ± 20·3	271 ± 12·8	249 ± 9	240 ± 18·8
Elongation-to-break (%)	33·6 ± 2·3	21·3 ± 5·5	47·7 ± 7·1	34·3 ± 6	54·4 ± 8·9	34·4 ± 6·3
Young's modulus (g mm^{-1})	32·9 ± 0·5	33·3 ± 1·4	31·1 ± 2·1	31·3 ± 0·6	30·3 ± 1·4	30·4 ± 0·9
Strength (g den^{-1})	3·8 ± 0·1	3·9 ± 0·2	3·9 ± 0·3	3·9 ± 0·2	3·6 ± 0·1	3·4 ± 0·3
1% stress (g)	27·2 ± 0·7	27·4 ± 1	29·9 ± 1·9	30·9 ± 0·6	29·5 ± 2·2	29·7 ± 1·3
2% stress (g)	50·7 ± 0·9	51·1 ± 2	52·2 ± 3·3	52·7 ± 0·8	51·3 ± 3·2	51 ± 2

[a] Yarns formed into one knot.

The tensile testing results, summarized in Table 2, show no marked differences between pure iPP and iPP/HOCP yarns. In fact, increasing the HOCP content of the yarn causes only a slight increase in the elongation-to-break parameter value.

Table 3 shows the influence of dry-heat setting (30 min): up to 70°C, shrinkage of the yarns was not affected by the composition, but in the range 70–100°C shrinkage increased with increasing HOCP content. It was also observed that the shrinkage in wet-heat (98°C for 1 h in water) is 3·6% for pure iPP yarn and 5·7% for iPP/HOCP yarn.

Viscoelastic properties

Typical curves of tan δ and E' versus temperature for iPP and iPP/HOCP yarns are shown in Figs 1 and 2. The tan δ versus temperature curves

TABLE 3
Shrinkage (%) of iPP and iPP/HOCP Yarns

Treatment temperature (°C)	*iPP*	*iPP/HOCP*	
		90/10	*85/15*
60	0·8	0·6	0·6
70	1·2	1·2	1·3
80	1·5	1·9	2·0
90	2·0	2·9	2·9
100	2·1	3·3	3·4

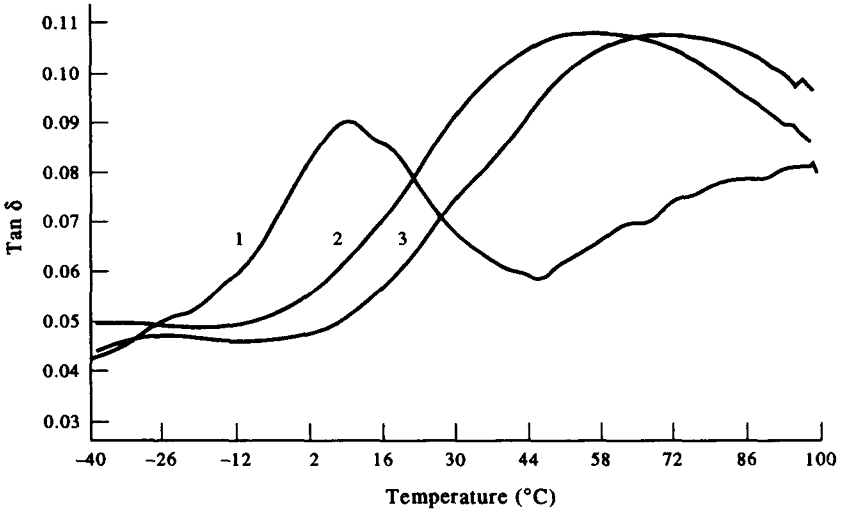

Fig. 1. Loss modulus (tan δ) as a function of temperature of iPP and iPP/HOCP yarns: (1) iPP; (2) iPP/HOCP 90/10; (3) iPP/HOCP 85/15.

(Fig. 1) have a single maximum that appears to shift to higher temperature with increasing HOCP content. Such behavior confirms the presence of a single amorphous phase with a T_g value that increases with increasing HOCP content.

In agreement with the tan δ trend, the E' values for blends begin to decrease at temperatures higher than those for iPP (Fig. 2); at temperatures

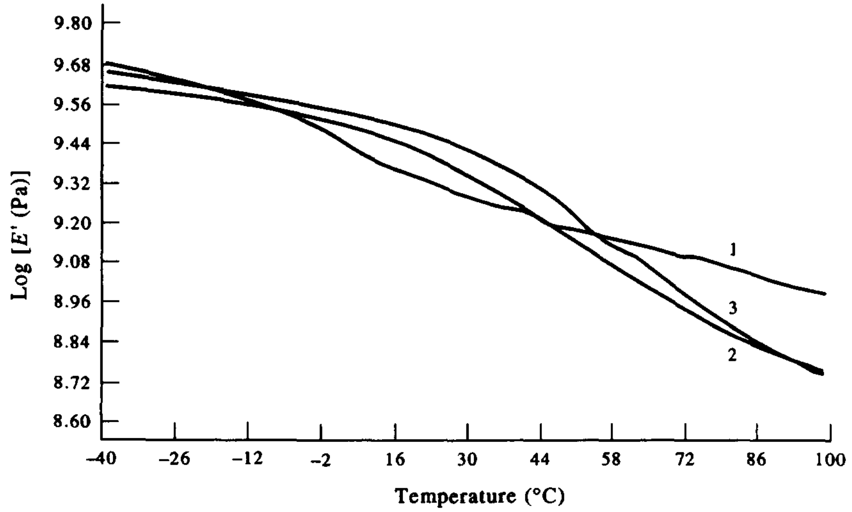

Fig. 2. Storage modulus (E') as a function of temperature of iPP and iPP/HOCP yarns: (1) iPP; (2) iPP/HOCP 90/10; (3) iPP/HOCP 85/15.

lower than about 40°C the E' values for blends are higher than those for iPP, while at temperatures higher than about 60°C the E' values for blends are lower than those for iPP. This behavior can be explained by assuming that when the amorphous phase of blend is in the glassy state, the presence of HOCP causes an increase of rigidity, while at high temperatures, where the amorphous phase is in rubbery conditions, the HOCP acts as a plasticizer.

The plasticizing effect occurring at high temperature is probably due to two concomitant effects:

(1) decrease of the overall crystallinity, and therefore increase of the fraction of material in the rubbery state;
(2) increase in the fluidity of the homogeneous amorphous phase due to the HOCP low viscosity (since viscosity is an additive property of blends).

Dyeing

The dye uptake of CI Disperse Red 13 and/or of CI Disperse Blue 3, increases with the HOCP content in the fiber when the dyeing approaches the equilibrium state (after 1 h at 98°C). Uptakes of CI Disperse Red 13 were 0·64%, 0·83% and 0·86% for 100/0, 90/10 and 85/15, respectively; for CI Disperse Blue 3, the values were 0·65%, 0·81% and 0·82% respectively. The transient dye uptake (at the start of dyeing) did not differ for the three fibers.

The greater uptake of dye by blends may be explained considering that:

(1) the decrease of the overall crystallinity increases the fraction of rubbery state material in which the dye has to fix;
(2) the higher fluidity (at 98°C) of the homogeneous amorphous phase promotes the diffusion process of dye to fibers.

If unsaturated oligocyclopentadiene (UOCP) is used instead of HOCP the uptake of dye is even better, as shown by some preliminary experiments; in such a case, the presence of unsaturation probably increases the affinity of the dye for fibers.

The reflectances for iPP, 90/10 and 85/15 blend fabrics dyed with CI Disperse Red 13, washed in water and dried, were 82% and 70%, respectively, taking up to 100% the reflectance of the pure iPP. Similar results were obtained by using CI Disperse Yellow 5 and CI Disperse Blue 3. The decrease of reflectance with increasing HOCP content confirms that, after washing, the quantity of the dye in the fibers was greater for blends than for pure iPP.

TABLE 4
Light, Wet-Washing and Dry-Cleaning Fastnesses of iPP, iPP/HOCP and PET Yarns

Dyes	*iPP*		*iPP/HOCP 90/10*		*iPP/HOCP 85/15*		*PET*	
	Red 13	*Blue 3*	*Red 13*	*Blue 3*	*Red 13*	*Blue 3*	*Red 13*	*Blue 3*
Light	1–2	2–3	4	5	4	5	4	4–5
Wet-washing (40°C)	3–4	4	4–5	4–5	5	5	5	5
Wet-washing (60°C)	3–4	3–4	4	4	4	4–5	4	4–5
Wet-washing (90°C)	1–2	1–2	1–2	1–2	1–2	1–2	4–5	4
Dry-cleaning[a]	1–2	1–2	4	3–4	4	3–4	—	—

[a] Petroleum spirit.

Light, wet-washing and dry-cleaning fastness

Table 4 shows the light, wet-washing and dry-cleaning fastnesses of iPP/HOCP fabrics, and also of PET as reference; it is apparent that both the wet-washing fastness at 40 and 60°C, and the light and dry-cleaning fastness of blends, are higher than those of pure iPP; this effect is probably due to the rise in T_g of the amorphous phase of the blends; in fact, at these temperatures, the amorphous phase of the blends is in the glassy state, so that the reduced molecular mobility protects the dye from degradation by light and slows down the kinetics of dye diffusion from the polymeric matrix to the aqueous bath.

It can be noted that the wet-washing fastness at 90°C for blends is poor, as is that for pure iPP. This may be explained in two ways; first, the high molecular mobility in the rubbery amorphous phase allows the dye to diffuse from the polymeric matrix to the wash liquor, and second, consideration may be given to a different amorphous phase microstructure of the blends. Essentially, two models have been proposed to explain the mechanism of dye migration from film and fiber substrates, the 'pore' and the 'free volume' models.[9]

The pore model is based on the hypothesis that the fibers, under dyeing conditions, are solids containing networks of channels or pores filled with solutions; the dye molecules diffuse into these pores and will be adsorbed onto the pores' surfaces. In the free volume model, the diffusion of the dye is considered to occur only because of the thermal motion of polymer segments in the amorphous zone.

Previous work[10] suggested the prevailing role in iPP films of the pore model with respect to the free volume model, and that an increase in crystallinity causes an increase in the microporosity of the amorphous phase. The limited fastness to light, washing and dry-cleaning confirms the prevalence of the pore model in pure iPP fiber. The increase in fastness of iPP/HOCP fibers with respect to pure iPP fiber could be explained by a decrease in microporosity, due to decrease in crystallinity, or by a prevalence of the free volume model.

CONCLUSION

Industrial fibers obtained by blending polypropylene with 10–15% of HOCP have equal spinnability and similar mechanical properties to pure iPP fiber.

The dyeing experiments showed that uptake of the dye from the dyebath was greater for the blends than for pure iPP. This increased uptake of dye is probably due to the decrease of the overall crystallinity, and to increase in fluidity caused by the HOCP.

Light fastness, wet-washing fastness (at 40 and 60°C) and dry-cleaning fastness of the new fibers are better than those of pure iPP fibers and are comparable with those of PET fibers; this effect is due to the reduced molecular mobility resulting from the higher T_g of the blends; the decrease of molecular mobility in the amorphous phase of blends protects the dye from degradation by light, and slows down the kinetics of dye diffusion from the polymeric matrix to the washing medium (water or petroleum spirit).

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