Production and characterisation of multifilament yarns made from polypropylene containing small amounts of oxidised polypropylene

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In the present work, oxidation of fibre grade polypropylene granules in the melt phase using oxygen gas has been performed. Then, virgin polypropylene granules were mixed with up to 10% by weight of oxidised granules and multifilament yarns from the blends were spun by a pilot-plant melt spinning machine. The characterisation of as-spun yarns was performed by FTIR and DSC analysis. Also the density, shrinkage and mechanical properties of the samples were evaluated. The results show that the as-spun blend fibre containing 10% by weight of oxidised polypropylene has the lowest crystallinity, density and melting temperature while it shows the highest shrinkage and mechanical property faults.

Keywords: polypropylene, oxidation, multifilament yarns, polar groups, crystallinity

Polypropylene (PP) is a polymer with good mechanical properties which has been used in a wide range of applications. However, due to their apolar aliphatic structure, high crystallinity, high stereo-regularity and absence of any reactive site in the molecules, PP fibres have poor dyeability and water absorption.[1-3] To solve this problem several methods have been proposed[1-4]: copolymerisation of propylene with other monomers; grafting onto isotactic PP; blending with other dyeable polymer before extrusion; dissolving or dispersing additives of low molecular weight in the polymer melt; and treatments to modify the surface of the filament after extrusion.

In last technique, one of the modification methods is oxidation. Due to the presence of tertiary hydrogen atoms on PP, this polymer is susceptible to oxidation.[5] The oxidation of PP in solid phase is done in the reactions with ozone, γ-initiated, corona method, and UV ray or with chemical oxidising mixture.[6-10] The oxidation of PP leads to the formation of oxygen-containing groups, which greatly affect the surface polarity and the adhesion properties of the polymer.[11,12,13]

The present investigation deals with the formation of polar groups in PP fibres through blend fibre production from virgin PP granules and small amounts of oxidised polypropylene (OPP) granules. The thermal properties and some physical characterisation of the multifilament yarns have been studied.

Experimental

Materials

Commercial fibre grade PP granule, known as 512P, was obtained from the Sabic Co. (Saudi Arabia). This material is normally considered to be stable against weathering oxidation, since it contains the usual synergistic combination of antioxidants that are found in commercial granules.

Reagent grade chemicals were used for tests and other analytical procedures.

Oxidation procedure

Oxidation of PP granules was carried out in the molten state in an internal mixer (Brabander, Plasticord PLE 331) at 200 °C with a residence time of 1 h at 60 rpm. Dodecanol-1 (Prolabo, France) was used as an accelerator at 0.1 wt%. This procedure was based on earlier studies.[13] The extrudates were cooled in cold water and cut into granules.

Melt spinning

Melt spinning was performed under nitrogen gas on a Fourne-Automatic melt spinning unit (pilot plant). The virgin PP granules were mixed carefully with 1, 3, 5, 7 and 10% by weight of oxidised polypropylene (OPP) granules and then placed in the extruder. The yarn spinning parameters are shown in Table 1. The yarns have 36 filaments with circular cross-sections.

Table 1 Melt spinning conditions of as-spun multifilament yarns

Parameters	Values
Feed pump speed/RPM	15
Take up speed/m/min	2200
Melt temperature/°C	250
Yarn linear density (dtex)	140

Characterisation techniques

The melt flow index (MFI) of the granules (oxidised and virgin) was determined in accordance with ASTM D1238, at 230 °C under 2.16 kg. Each MFI value was the average of three determinations.

IR spectra were obtained with a Nicolet Fourier Transform Spectrophotometer with a resolution of 4 cm^{-1} (30 scans average) to confirm the presence of new groups in the blend fibres.

The bulk density of the as-spun fibres was determined by a density gradient column using a mixture of water and ethanol at 23 °C. The density reported (ρ) is an average of five density measurements. The crystalline fraction (X) of the samples was then estimated using the following expression:

$$X = \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \times \frac{\rho_c}{\rho} \qquad (1)$$

where ρ_c and ρ_a are densities of crystalline and amorphous polypropylene and were taken to be 0.9363 g/cm^3 and 0.8576 g/cm^3, respectively.[14]

Stress–strain curves were obtained using an Instron tensile tester model 5566 H1730. A gauge length of 100 mm and cross-head speed of 1000 mm/min were employed. From stress–strain plots, the modulus, tenacity, percentage extension at break and work of rupture were evaluated. Ten specimens were tested in each experiment and the reported data are the statistical average of the 10 specimens.

A Perkin-Elmer differential scanning calorimeter (Model DSC7), with nitrogen purge, was used to analyse the thermal behaviour of the multifilament yarns. The samples consisted of approximately 7–8 mg of finely chopped fibres in aluminum pans. Thermograms were recorded in three consecutive runs: (i) a first heating, from 40 to 210 °C and held for 5 min to remove residual crystals, followed by (ii) cooling from 210 to 40 °C, and finally (iii) a second heating, from 40 to 210 °C. All experiments were performed at a heating/cooling rate of 10 °C/min. The equipment was calibrated with indium. From the heat of fusion, an apparent crystallinity (X) was determined by following equation:

$$X(\%) = (\Delta H/\Delta H^*) \times 100 \qquad (2)$$

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Table 2 MFI for virgin and oxidised PP granules

	Virgin granule	Oxidised granules
MFI/g/10min	24.43	30.55
	24.22	29.80
	24.82	29.23
Average	24.49	29.86
CV%	1.23	2.22

where ΔH is the measured melting enthalpy and ΔH^* is the enthalpy of fusion of a 100% crystalline polypropylene, that is 209 J/g.[14]

The fibres were freely suspended in boiling water for a specific time to determine shrinkage values. The initial and final lengths were measured at room temperature, and the shrinkage calculated as the percentage change in length relative to the initial length.

Both neat PP fibre and blend fibres were subjected to a staining technique for the detection of polar sites in fibres. Samples were immersed in a solution containing isopropanol, Sudan Ш, methylene blue and ammonium hydroxide for 10 min at boiling temperature. This solution was prepared according to former study.[15] After this time, the samples were withdrawn from solution, rinsed with isopropanol and distilled water and dried with tissue paper.

Results and discussion

MFI of granules

It can be seen from Table 2 that the MFI (melt flow index) of OPP (oxidised PP) granules is higher than that of virgin PP granules. Previous studies have shown that the oxidation of PP involves mainly chain scission and decreases the molecular weight.[11–13] This explains the increase of MFI in the OPP granules.

Characterisation by IR spectroscopy

The FTIR spectra of PP granules obtained after oxidation present several broad overlapped absorption bands. These correspond to products having –OH (alcohol, hydroperoxides, acids, *etc.*, at 3200–3600 cm^{-1}) and >C=O groups (ketones, acids, esters *etc.*, at 1700–1800 cm^{-1}). Also a significant increase in COX species (at 1220–1700 cm^{-1}) is observed.[11–13] However, it is impossible to establish more precisely the exact nature and relative contribution of each species from these spectra. Figure 1 shows the FTIR spectra of fibre samples in the range of 1600–1850 cm^{-1}.

In these plots there is a broad absorption band centred at 1732 cm^{-1}.

Figure 2 presents the FTIR spectra of multifilament yarns in the range of 3200–3700 cm^{-1}. One large vibrational band due to the OH group stretches in the blend fibres is centred at 3400 cm^{-1}. In polyblend fibres, as OPP is added, the peak intensity at this absorbance shifts gradually to higher intensities and the maximum absorbance occurs in the as-spun blend sample containing 10% by weight of OPP. Changes in the intensities, shape, and position of C=O, OH, and COX stretching modes are associated with the interaction between OPP and PP.

It is necessary to normalise the carbonyl, hydroxyl and COX species absorption band by a reference band (2722 cm^{-1}) to allow for sample to sample variations as can be seen in Table 3. This reference peak was chosen from an earlier study.[16]

Figures 3–5 are plots of the COX species, carbonyl and hydroxyl indices versus OPP fraction in blend fibres. It is observed from Fig. 3 that by increasing the OPP fraction in blend fibres up to 5%, the COX species indices changes are negligible. As can be seen in Figs 4 and 5 and Table 3 the absorbance ratios of carbonyl and hydroxyl groups increase with rising OPP fraction in the blend fibres. It is clear from these figures, that the carbonyl and hydroxyl indices difference, between the blend containing 1% by weight of OPP and neat

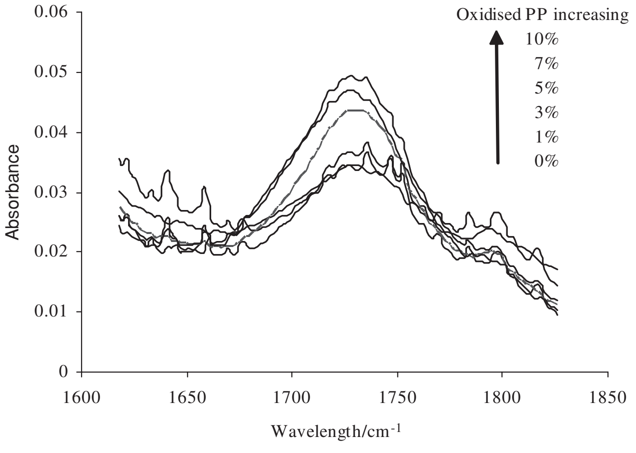

Fig. 1 IR spectrum of virgin PP Fibre and PP/OPP blend fibres in the range of 1600–1850 cm^{-1}.

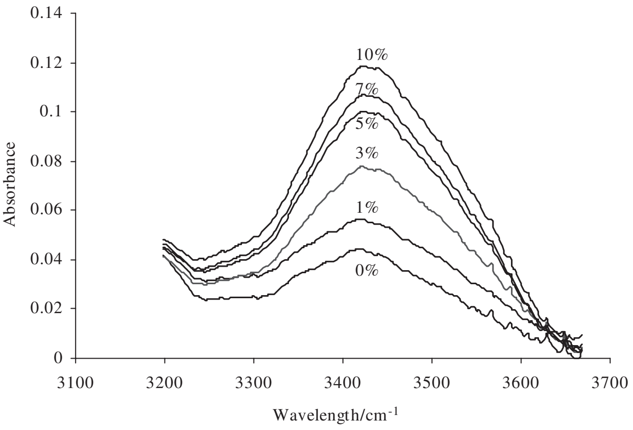

Fig. 2 IR spectra of virgin PP fibre and PP/OPP blend fibres in the range of 3200–3700 cm^{-1}.

Table 3 The values of normalised absorption band of carbonyl, hydroxyl and COX species, isotacticity and crystallinity of samples obtained from FTIR spectra

Sample	A(1167/2722 cm^{-1})	A(1732/2722 cm^{-1})	A(3420/2722 cm^{-1})	Isotacticity/%	Crystallinity/%
100/0 (PP/OPP)	2.073	≅ 0	≅ 0	92.11	48.08
99/1 (PP/OPP)	2.217	≅ 0	0.053	90.58	47.14
97/3 (PP/OPP)	2.236	0.562	1.065	91.72	49.37
95/5 (PP/OPP)	2.237	0.580	1.271	91.30	49.05
93/7 (PP/OPP)	2.309	0.661	1.507	92.41	48.86
90/10 (PP/OPP)	2.434	0.697	1.565	89.90	46.71

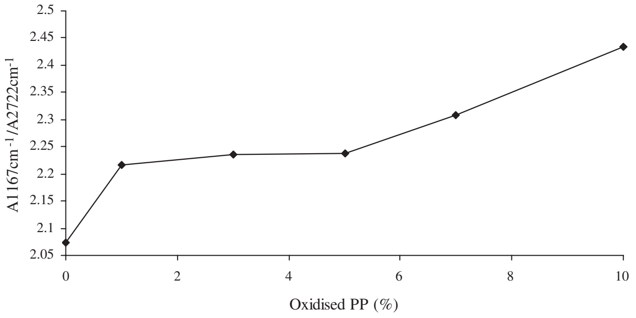

Fig. 3 Effect of OPP fraction in filament yarns on COX species normalised absorption band.

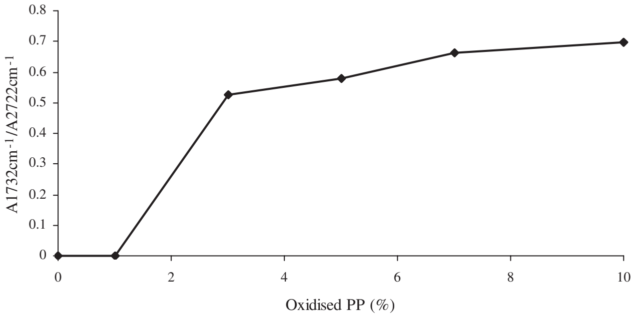

Fig. 4 Effect of OPP fraction in filament yarns on carbonyl normalised absorption band.

PP fibre, is minor, but by increasing the OPP fraction to 3% the normalised absorption increased significantly. Note that the blend fibre containing 10% by weight of OPP has maximum carbonyl, hydroxyl and COX absorption indices. It is also found from Figs 4 and 5 that the contribution of OH groups is much more important compared to the carbonyl region.

The isotacticity values of filament yarns were also estimated from FTIR measurements through the ratio of R= A_{997}cm^{-1}/A_{972}cm^{-1} and are shown in Table 3.[17,18] As can be seen from Table 3 the isotacticity of samples did not present significant variations, but the blend sample containing 10% by weight of OPP has least isotacticity. The crystalline fraction of samples was also evaluated from two specific peaks (997 and 972 cm^{-1}) and one reference peak (2722 cm^{-1}):[19,20]

$$X_C(\%)=[109\left(\frac{A_{997}-A_{2722}}{A_{972}-A_{2722}}\right)-31.4]\,100 \qquad (3)$$

where A is the absorbance.

The data in Table 3 show that as the amount of OPP in blends increased the crystalline fraction of samples did not show specific trend. The least crystallinity was observed in the blend sample containing 10% by weight of OPP. As can be seen from Fig. 6 the crystallinity of fibre samples follows a similar trend to that which has been discussed for isotacticity.

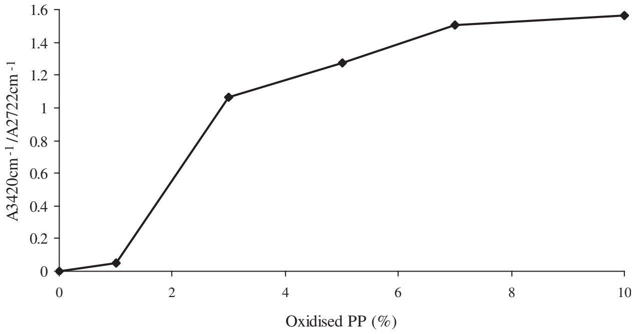

Fig. 5 Effect of OPP fraction in filament yarns on hydroxyl normalised absorption band.

Density

Perhaps one of the most obvious effects brought about by the blending is on the density of blends. Fig. 7 shows the influence of OPP fraction in fibres on the density and the calculated crystalline fraction from the density measurements. As can be seen from Fig. 7 the blend samples register a decrease in density on increasing OPP fraction in the blend fibres because of reduced compactness or packing of PP molecules in the polyblend fibres due to the presence of the dispersed OPP phase. The density and crystalline fraction of blend fibres containing 10% by weight of oxidised PP is less than that of the other samples. The crystallinity value of this sample is about 23% lower than the ones of neat PP fibre. The decrease in crystalline fraction of blend fibres can be attributed to chemical irregularities, presence of new chemical groups in blend fibres and the decrease of molecules in the helical conformation, shown by the decrease in the isotacticity index.

Mechanical properties

Table 4 shows the mechanical characteristics of multifilament yarns. The changes in the as-spun fibres mechanical properties are presented in percent retained which is calculated according to following equation:

$$\%\ \text{Retained} = \frac{\text{test value of samples}}{\text{test value of virgin PP fibre}} \times 100 \qquad (4)$$

Figure 8 displays the changes in mechanical properties of fibres with and without oxidised polypropylene. The decrease

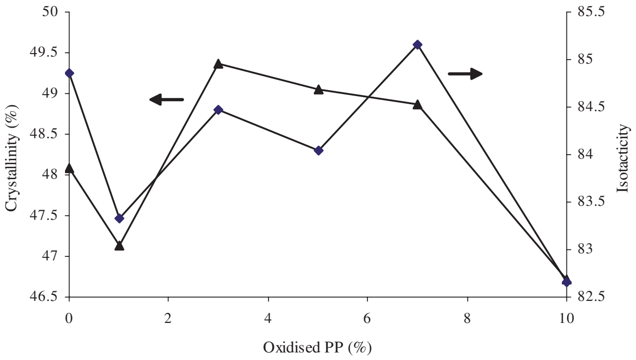

Fig. 6 Effects of OPP fraction in filament yarns on crystallinity and isotacticity measured from FTIR spectra.

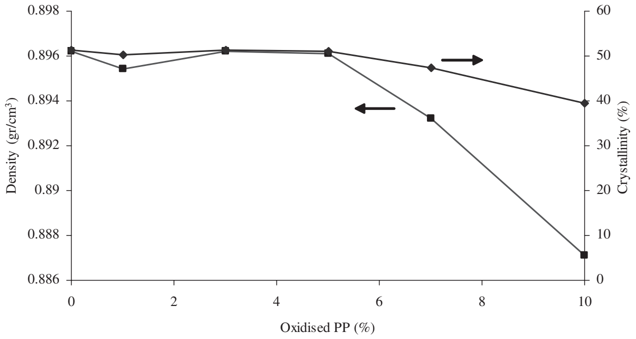

Fig. 7 Effects of wt% fraction of OPP on density and the calculated crystalline fraction of filament yarns.

Table 4 Mechanical properties of neat PP fibre and polyblend samples

Sample	Tenacity (cN/dtex)	Elongation at break/%	Specific work of rupture (cN/dtex)	Initial modulus (cN/dtex)
100/0	2.33[a]	178.49	2.94	9.71
(PP/OPP)	(5.60)	(12.11)	(16.54)	(5.31)
99/1	2.25	177.34	2.75	8.92
(PP/OPP)	(11.22)	(7.54)	(6.13)	(14.34)
97/3	2.13	165.43	2.48	8.81
(PP/OPP)	(9.64)	(7.67)	(9.05)	(9.13)
95/5	2.12	160.56	2.40	8.78
(PP/OPP)	(15.14)	(14.12)	(13.10)	(15.76)
93/7	2.05	160.15	2.22	8.10
(PP/OPP)	(7.51)	(6.17)	(18.15)	(13.43)
90/10	1.94	154.78	2.11	7.78
(PP/OPP)	(8.71)	(4.75)	(14.64)	(10.19)

[a] Average, (the numbers in parentheses are CV %).

in tenacity of blend samples coordinates with the amount of carbonyl and hydroxyl groups in the blend fibres. As can be seen in Fig. 8 the tenacity of filament yarn containing 10% by weight of OPP is about 17% lower than that of the neat PP fibre. In general, diminishing the degree of isotacticity decreases the tensile strength of multifilament yarns and as mentioned before (Table 3) the blend fibre containing 10% by weight of OPP has the least isotacticity; therefore this sample has least tenacity.

In blend samples, the presence of OPP produced weak points and stress concentration in these regions during tensile testing caused the fibre to break unexpectedly (decreasing elongation at break) and under low tension (decreasing tensile strength). The reduction in elongation at the break of the blend fibres is also due to restriction of chain mobility thanks to the OPP. It should be noted that blending of OPP which has lower molecular weight with PP and creating polar groups such as carbonyl in polyblend fibres reduces the chain entanglement density of PP; therefore, lower stress is needed for the separation of lamellae.

As can be seen from Fig. 8 by increasing the OPP fraction in polyblend fibres the elongation at break decreased. It should be noted that drastic decrease did not occur in the mechanical properties; therefore it can be said that the tensile properties are still acceptable. Fig. 8 shows that the most decrease occurred in the specific work of rupture of the blends. Work of rupture is defined as the area under the stress – strain curve. As a result, the sensitivity of the work of rupture to OPP presence in the blend fibres is higher compared to elongation at break or load at break. One of the most important factors affecting the tensile modulus of PP filament yarns is crystallinity. As previously shown (Density discussion) the crystallinity of blend fibres did not change significantly; hence the change in tensile modulus of blend samples is negligible.

Thermal analysis

The results of the DSC tests on different samples are summarised in Table 5. As can be seen, the melting temperature and crystalline fraction of the blend fibres was not affected considerably by the increasing OPP fraction.

Decrease in the onset of first melting was observed by increasing the OPP fraction in blend fibres. The least crystalline fraction and melting temperature were seen in the blend fibre containing 10% by weight of OPP. It has been found that the decrease in the melting temperature can be due to disruption of order regions but this may not apply here because there was no strong evidence of reduction in crystallinity in blend fibres. Therefore, a slight decrease in melting temperature can be attributed to crystalline decrease, the presence of small and less regular lamella and more defect crystals in the blend fibres' structure. Figures 9 and 10 display representative thermograms of multifilament yarns during the first and second heating runs, respectively.

As can be seen in Fig. 9 during first heating only the neat PP fibre shows a single peak whereas the blend samples exhibit multiple peaks. There are numerous reports of the occurrence of double endotherms during DSC experiments. In the current work, it is speculated that the double melting peaks may be due to one of the following reasons: (i) melting of crystals with different melting points, (ii) chain irregularity due to the presence of carbonyl groups and

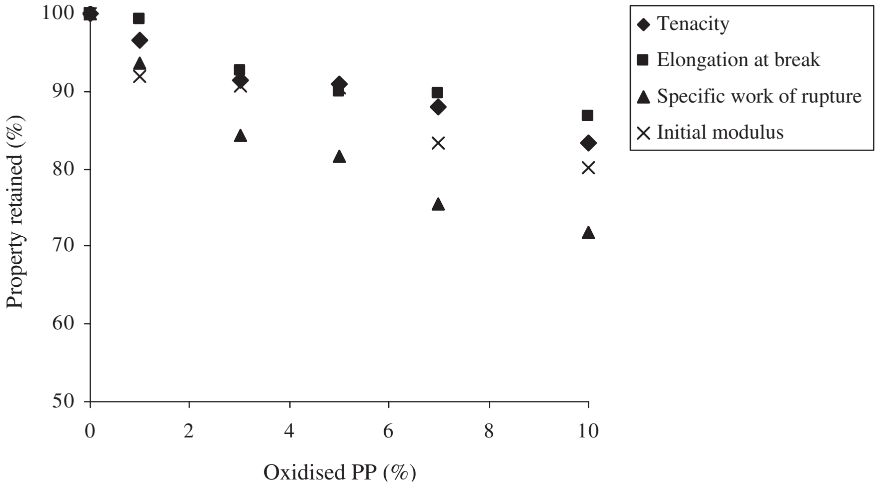

Fig. 8 Changes in mechanical properties of filament yarns as function wt% fraction of OPP.

Table 5 Values obtained from the DSC curves of the filament yarns and calculated crystallinity

Sample	Heating								Cooling		
	1st cycle				2nd cycle						
	Onset of melting/°C	T_{m1}/°C	ΔH_m/J/g)	Crystallinity /%	Onset of melting/°C	T_{m2}/°C)	ΔH_m/J/g	Crystallinity /%	T_c/°C	ΔH_c/J/g	Crystallinity /%
100/0 (PP/OPP)	140.86	163.50	86.19	41.23	131.05	161.51	84.40	40.38	115.58	94.57	45.24
99/1 (PP/OPP)	132.98	159.05	85.47	40.89	119.24	159.82	82.82	39.62	114.61	88.72	42.44
97/3 (PP/OPP)	132.98	158.94	83.63	40.01	119.94	159.90	81.37	38.93	115.25	87.32	41.77
95/5 (PP/OPP)	133.86	165.29	85.11	40.72	119.94	160.22	83.48	39.94	114.96	89.70	42.91
93/7 (PP/OPP)	130.31	159.45	81.25	38.87	112.54	155.03	84.72	40.53	114.92	85.52	40.91
90/10 (PP/OPP)	130.31	158.73	79.86	38.21	123.50	159.59	78.11	37.37	114.52	82.86	39.64

Table 6 Shrinkage percentage of PP and polyblend fibres in boiling water

Sample	100/0 (PP/OPP)	99/1 (PP/OPP)	97/3 (PP/OPP)	95/5 (PP/OPP)	93/7 (PP/OPP)	90/10 (PP/OPP)
Shrinkage/%	1.88[a] (1.30)	1.56 (1.80)	1.70 (1.90)	4.33 (2.30)	4.52 (1.70)	6.04 (1.70)

[a]Average, (the numbers in parentheses are CV %)

hydroperoxides, or (iii) recrystallisation or rearrangement of structure during heating.[21,22]

The second heating curves of DSC endotherms of the blend fibres have been shown in Fig. 10. As can be seen, two peaks were observed for the blend fibres' endotherms, a strong peak at 160 °C and a weak peak at 145 °C. A possible cause for the additional peaks is that more than one type of crystal formed because of the influence of OPP on the crystallisation of PP on the DSC cooling run. Another possibility is the independent crystallisation of OPP in blend fibres on the DSC cooling run; on subsequent heating it appeared as additional peaks. In all samples, the cooling curves show a single exotherm (has not been shown here). As can be seen in Table 5 no specific trend was shown in T_c and ΔH_c. It is proved that the long molecules will crystallise first if the system can reach equilibrium during cooling process.[21,22] However, the fast cooling rate eliminates the difference on the crystallisation ability and both the long and short molecules crystallise at the same temperature range. In the cooling run the crystallinity of the blend fibre containing 10% by weight of OPP was lower than that of the neat polypropylene fibre. This occurred possibly because of the OPP dissolved in the PP, which hindered the crystallisation of PP. Also Table 5 shows that the second melting point (T_{m2}) did not change significantly by increasing the OPP fraction in the blend fibres.

Shrinkage

The results of shrinkage experiments in boiling water are given in Table 6. This Table shows that, although no considerable difference was observed between the shrinkage of virgin PP fibre and polyblend fibres containing 1% and 3% by weight of OPP, on further increase of OPP, shrinkage of blend fibres also increased. The blend fibre containing 10% by weight of OPP has the highest shrinkage value and it seems that significant structural changes in blend samples have not occurred. As can be seen in Fig. 11 the shrinkage behaviour of multifilament yarns is in good agreement with the crystallinity trend.

Staining

The results of staining experiments were evaluated just by observation. Generally, methylene blue stains the polar component domains and Sudan III (red dye) stains the apolar ones.[15] The virgin PP fibre displayed a pink discoloration but the blend fibres acquired complex blue and pink areas and distribution of blue dye is non-uniform. This shows that there is separation between oxidised and non-oxidised material. If carbonyl groups induced due to oxidation, are expected to be stained a basic dye *e.g.* methylene blue, results indicate that the blend fibre containing 10% by weight of OPP has more affinity to methylene blue as compared to other samples. The polyblend fibre containing 1% by weight of OPP shows only a small blue area (the rest is pink). This trial confirms the presence of carbonyl and hydroxyl groups in the blend fibres.

Conclusion

Mixing of polypropylene granules and small amounts of oxidised polypropylene granules produced filament yarns containing polar groups. It has been found that by increasing

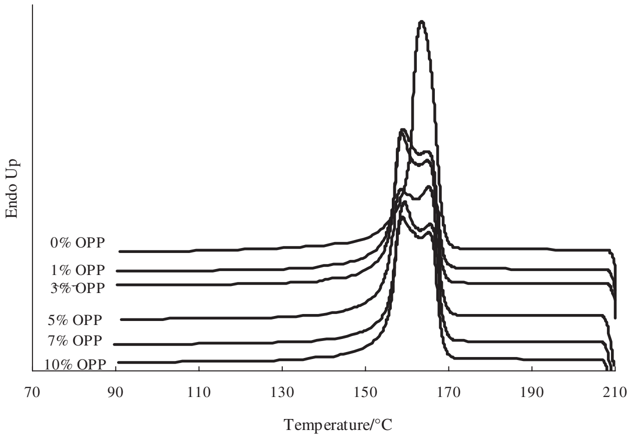

Fig. 9 First heating cycles of DSC thermograms for neat PP fibre and polyblend fibres.

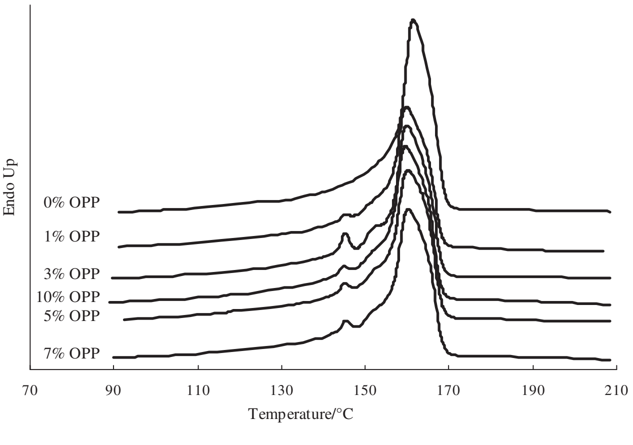

Fig. 10 Second heating cycles of DSC thermograms for neat PP fibre and polyblend fibres.

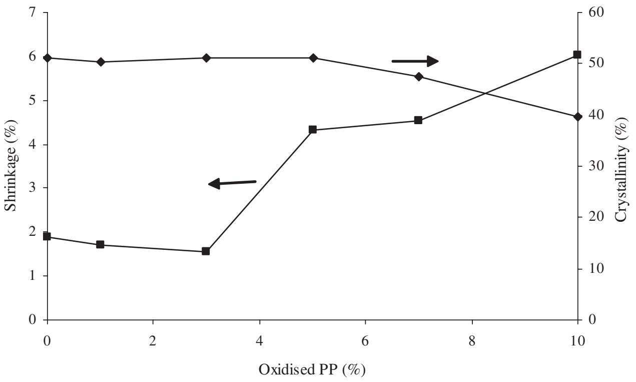

Fig. 11 Shrinkage and crystallinity (calculated from density method) versus of wt% fraction of OPP for neat PP fibre and polyblend fibres.

the amount of oxidised polypropylene in blend fibres the absorbance intensity of polar groups (carbonyls and hydroxyls) increased. According to the data available from the DSC curves, the thermal properties of PP and polyblend fibres are similar. The mechanical properties of PP/OPP blend fibres exhibit a drop in comparison to neat PP fibre, but are still acceptable. The density and calculated crystallinity of the blend yarns are lower than that of the neat PP fibre. The shrinkage values of the samples show good agreement with crystallinity results.

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