Polypropylene / Poly(Trimethylene Terephthalate) Meltblend Fibres With Enhanced Dyeability.

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Abstract

Polypropylene (PP) based polymer alloy fibres consisting of varying quantity (5-20%) of polytrimethylene terapthalate (PTT) were meltspun to modify PP structure. The compatibility of blends, crystallization behaviour and structural changes of fibres were analyzed using wide angle X-ray diffraction, differential scanning calorimetry, birefringence, tensile properties and thermal stability. The polyblend fibres exhibited increased dyeability with increase in PTT content along with excellent wash and light fastness properties. The structure of modified blend fibre is compared with that of the pure PP fibre and the enhanced dyeability is discussed in the light of changes in internal structure of the blend fibres.

1. Introduction

Polypropylene (PP) fibres have wide application due to a favourable combination of processability, physical / chemical properties and price. However, due to its inert chemical nature and highly crystalline structure, PP fibre poses difficulty in chemical processing and dyeing while using conventional techniques. Therefore PP fibres need to be modified altering either its chemical and/or physical structure [1-3].

Polyblending has been a successful technique to modify PP and improve the fibre's physico-chemical properties for improved dyeability. Polyblend fibres are produced by melt blending two or more different polymers depending upon the properties to be imparted and spun into filaments. PP has been made disperse dyeable by forming composite fibres with polyester [4,5]. Among polyester, polytrimethylene terapthalate (PTT) exhibits favourable characteristics of both polyethylene terephthalate (PET) (i.e. mechanical properties) and polybutylene terephthalate (PBT) (i.e. processability) and considered superior in terms of its disperse dyeability as it exhibits atmospheric disperse dyeing with excellent colour fastness.[6]

Shu Y.C et al.[7] have reported the preparation and physical properties of metallocene isotactic polypropylene / PTT conjugated fibres and Marcincin A et al. [8] studied the rheological properties, phase structure and mechanical properties of PP/PTT polyblend fibres wherein PTT component was 30 and 70% in the blend. However, the behaviour of PP/PTT blend using much lower concentrations of PTT in the blend formation needs to be studied to understand the fibre processing, structural changes and its interrelationship with dyeability properties.

In our previous work, polyblend PP based fibres were made disperse dyeable by meltblending PP with cationic dyeable polyester (CDPET), carrier free dyeable polyester (PBT), polymethyl methacrylate (PMMA) and polystyrene (PS) [5,9]. In our present work thus PP/PTT polyblend fibres were meltspun using 5-20% PTT as a minor polymer and the behaviour of the blend fibres with respect to compatibility, thermal properties, crystallization behaviour, mechanical properties and dyeability, etc is discussed here.

2. Experimental

2.1 Materials

Polypropylene chips (PP) Repol H350FG, having MFI 35 were supplied by Reliance Industries Ltd, India where as Futura clear polytrimethylene terapthalate (PTT) having 0.93 IV were supplied by Futura Polymers, India.

Following disperse dyes were supplied by Dystar India Pvt. Ltd.

- Dianix Blue ER (CI number DsB 63), Low Energy.
- Dianix Yellow S-6E ER (CI number DsY 114), Medium Energy
- Dianix Rubine S-2G 150% (CI number DsR 167.1), High Energy.

2.2 Fibre spinning

PTT was predried at 120^{0}C for 24 h and melt blending with different PP/PTT ratios was carried out using a co-rotating twin-screw extruder (APV Baker, UK). The barrel temperatures ranged from 210 to 255^{0}C, and the screw speed was 60 rpm. The extruded pellets were dried in an oven at 120^{0}C for at least 12 h, before melt-spinning.

The melt spinning of compounded chips was carried out on a laboratory melt spin extruder (Fair Deal Associates, India). The temperatures of the extruder zones ranged from 180 – 270^{0}C. In the extruder zone, the chips melted to form a molten mass which then moved further to a metering pump and the filaments extruded from the spinneret were cooled down by blowing cool air in a 1.5 meter quench duct. The filaments were guided to the godet roller via a metered spin finish passage, which were subsequently taken over to the draw rollers. The drawing was carried out by two-stage drawing method at previously optimized draw ratio.

2.3 Dyeing of fibres

The fibres were pre-scoured with 2 g/l of a nonionic detergent at 70^{0}C for 30 min and subsequently rinsed with hot and cold water and then dried in air. The disperse dyeing of the pre-scoured fibres was carried out in a high temperature / high pressure beaker dyeing machine using a standard method of the dyeing of synthetic fibres. The dyed samples were then subjected to reduction clearing treatment for 20 min at 70^{0}C with 2 g/l caustic soda and 2 g/l sodium hydrosulphite, followed by neutralization with 1 g/l acetic acid solution, washing and drying.

3. Characterization of fibres

3.1. Thermal analysis

The thermal properties and crystallization behaviour were studied using differential scanning calorimetry (Shimadzu, Japan). The measurements were carried under nitrogen atmosphere (flow rate 20 ml/min). Crystallization exotherms and melting endotherms were recorded and the degree of crystallinity (X) was calculated from the DSC data using the following relationship:

$$X = \frac{\Delta \mathrm{He}}{\Delta \mathrm{H}_c^0} \times 100$$

where, ΔH_e is experimental heat of fusion and ΔH^0_c is the heat of fusion for a 100% crystalline polymer. Values of ΔH^0_c taken from the literature, are 145.48 J/g for PTT [10] and 207 J/g for PP [11], respectively.

3.2. X-ray diffraction studies

X-ray diffraction studies were carried out using powder technique on a Bruker D8 advance X-ray diffractometer (USA) using CuKα radiation. Information on crystalline form and percentage crystallinity was obtained from the I-2θ plots.

3.3. Birefringence

The birefringence values for the various fibre samples were obtained with the help of polarizing microscope fitted with Bereck compensator by retardation method [12].

3.4. Thermogravimetric analysis

The thermal stability of the samples was studied by carrying out thermogravimetric analysis (TGA) using DTG-60H thermogravimetric analyzer (Shimadzu, Japan). Samples of about 7.5 mg were heated from 50 to 500 ^{0}C at a heating rate of 10 ^{0}C/min in a nitrogen atmosphere, and the corresponding degradation levels at various temperatures were noted.

3.5 Tensile properties

Tensile testing of filaments was carried out on Tinius Olsen tensile testing machine. The gauge length was 100 mm and strain rate was kept at 50 mm/min. Ten samples were tested and their average values are reported.

3.6. Evaluation of colour strength

Table 1. The melting behavior data of PP/PTT blend fibres obtained from DSC analysis

Fibre	**Onset temp (^{0}C)**		**Endset temp (^{0}C)**		**Melting peak (^{0}C)**		**Heat of melting (J/g)**		**Crystallinity (%)**
(PP:PTT)	**PP**	**PTT**	**PP**	**PTT**	**PP**	**PTT**	**PP**	**PTT**	
100:0	161.92	-	172.56	-	169.56	-	141.9	-	68.55
95:5	156.43	-	169.78	-	166.66	-	124.96	-	60.37
90:10	156.18	216.9	168.61	229.44	165.9	225.06	113.08	4.69	57.85
85:15	155.21	219.74	168.2	229.84	165.33	226.36	95.67	5.16	49.76
80:20	154.89	220.36	167.96	230.72	164.74	226.66	79.02	14.46	48.11

The dyed samples were evaluated for colour depth in terms of Kubelka Munk function (K/S), using Spectra Flash SF 300, computer colour-matching system, supplied by Datacolour International, USA [13]. Kubelka Munk function (K/S) is given by:

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where, R is reflectance at complete opacity, K is the absorption coefficient and S is scattering coefficient.

3.7. Evaluation of colour fastness

Colour fastness to washing was evaluated as per ISO 105-C10:2006 B washing fastness test conditions in a Launder-O-meter for 30 min at 60 ^{0}C, 5 g/l non-ionic soap and 2 g/l soda ash at a liquor to material ratio of 50:1. Colour fastness to light was evaluated as per BS 1006 test method. Dyed samples were placed on cardboard paper, and its half portion was covered by a black sheet of paper and remaining portion was exposed to mercury lamp continuously for 17 hrs. The fading of exposed samples was graded with reference to blue wool standards subjected to same testing conditions.

4. Results and discussion

4.1. Thermal behavior of polyblend fibres

Results of DSC analysis given in Table 1 indicate that ingenral two distinct melting peaks for PP/PTT blend are observed. In case of pure PP the melting peak was at 169.56^{0}C. At 5% PTT in meltblend fibre, the melting peak of PP shifts slightly to lower temp of 166.66^{0}C, whereas PTT melting peak is not visible, which indicates that PTT has been dispersed uniformly throughout the PP matrix. However, 10%, 15% and 20% PTT levels in meltblend fibres, clear melting peaks in temperature range of 225.06 to 226.66^{0}C appear, corresponding to the melting point of PTT. This clearly makes it evident that the PP/PTT blend is an immiscible blend, where in both the polymers show their clear identity. It is to be noted that PP is nonpolar polymer whereas PTT, has some degree of polarity due to the presence of –COOH groups and hence, the immiscibility of the blend is understandable. As the percentage of PTT in the PP/PTT blend increased, there was progressive decrease in crystallinity of the blend fibre. This is attributed to PTT polymeric chains consisting of aromatic units offering steric hinderance to close packing of PP chains

4.2. X-ray crystallinity studies of polyblend fibres

X-ray crystallinity studies were carried out on PP and two varieties of PP/PTT blends consisting of minimum (5%) and maximum (20%) PTT used in this study. The results in Fig 1 further confirm the findings obtained on DSC analysis, that with increase in PTT content in PP/PTT polymer blend, crystallinity decreased progressively from 62.72% for pure PP to 55.29% and 49.65% for 95:5 and 80:20 PP:PTT blends, respectively.

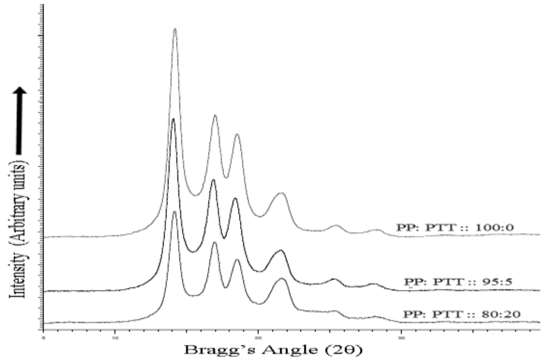

Figure 1. X-ray diffraction curves of PP/PTT blend fibres.

The I-2θ plots of the meltblend spun fibres show a gradual decrease in the intensity of the X-ray diffraction peaks suggesting there by increase in the amorphous content, as the PTT content increased which is quite obvious. At 20 % PTT in the blend, there appears a bulge from 23 – 25^0 (2θ), signifying the presence of PTT with imperfect crystal formation.

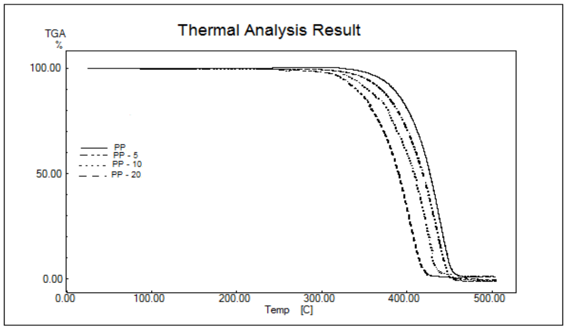

Figure 2. Thermogravimetric analysis of PP/PTT blend fibres.

4.3. Thermal Stability

Figure 2 and Table 2 representing TGA results for PP/PTT polymer blend fibres, reveal that the thermal stability of the blend fibres decreased progressively as PTT content in the blend increased, which may be attributed to decrease in crystallinity of the blend fibres. However, the blend fibres are found to be stable upto 350^0C for 20% PTT and their rapid degradation starts beyond 400^0C only, which is much higher than the regular processing temperature of fibres.

Table 2. TGA derived decomposition temperatures and weight loss

Fibre (PP:PTT)	Onset temp (^{0}C)	10% wt loss (^{0}C)	50% wt loss (^{0}C)	100% wt loss (^{0}C)
100:0	402	426	465	498
95:5	395	403	446	482
90:10	378	392	437	478
80:20	354	383	407	460

4.4. Tensile Property

As the content of PTT in the polymer blend increased, the tenacity was found to be decreasing progressively whereas elongation slightly increased. Results in Table 3 indicate that the tenacity of the pure PP was found to be maximum, which was obvious due to its highest crystallinity. The decrease in tenacity could be attributed to the fact that PP/PTT blend fibres forming immiscible blends exhibit progressive decrease in the crystallinity as the PTT content in the blend increased.

Table 3. The effect of PTT content on tensile properties of PP/PTT blend fibres

Fibre (PP:PTT)	Breaking force (gf)	Tenacity (gf/d)	Peak elongation (%)	Tenacity loss (%)
100:0	754.2	5.53	14.15	--
95:5	589.2	4.28	15.49	22.60
90:10	528.2	3.63	15.8	34.36
85:15	484.9	3.535	15.85	36.08
80:20	457.9	3.128	17.16	43.45

Also decrease in over all orientation (ref. Table 4) may also be responsible for decrease in tenacity. Hence depending upon the end application of such blend fibres, the extent of PTT content in PP/PTT blend can be controlled.

Table 4. Birefringence values of disperse dyed PP/PTT blend fibres

Fibre (PP:PTT)	Birefrengence
100:0	0.03128
95:5	0.02935
90:10	0.02853
85:15	0.02832
80:20	0.02657

4.5. Disperse dyeability

Results in Table 5 indicate very low K/S values (tinting) for 100% PP fibre, which is obvious due to its highly crystalline structure. However, as the PTT content in the blend increased, there was significant increase in K/S values.

Table 5. K/S values of disperse dyed PP/PTT blend fibres

Fibre (PP:PTT)	Dianix Blue ER	Dianix Yellow S-6E ER	Dianix Rubine S-2G 150%
100:0	1.6768 (100)	0.7392 (100)	2.4353 (100)
95:5	21.8629 (1203.8)	13.5902 (1738.5)	16.4481 (575.4)
90:10	28.8235 (1618.7)	19.0285 (2474.2)	25.3808 (942.2)
85:15	30.4743 (1717.2)	21.8838 (2860.5)	28.5842 (1073.7)
80:20	29.7207 (1672.2)	20.1944 (2631.9)	28.1288 (1055.1)

[a] Values in bracket represent percentage increase in K/S values over that of pure PP

Table 6. Light and washing fastness properties of disperse dyed PP/PTT blend fibres.

Fibre	**Light Fastness**			**Washing Fastness**		
(PP:PTT)	**Dianix Blue ER**	**Dianix Yellow S-6E ER**	**Dianix Rubine S-2G 150%**	**Dianix Blue ER**	**Dianix Yellow S-6E ER**	**Dianix Rubine S-2G 150%**
100:0	2-3	3	3	2	2	2
95:5	4	4	4	4	4	4
90:10	5	5	5	4	4	4
85:15	5	5	5	4	4	4
80:20	5	5	5	3	3	3

The increase in disperse dyeability can be attributed to significant decrease in crystallinity of meltblend fibres. Also overall orientation of the polymeric chain molecules also decreased as shown from the results of birefringence studies given in Table 4.

Both of these changes in internal structure of the PP/PTT blend thus resulted in enormous increase in K/S values and their dyeability. In general for all the three disperse dyes studied, the increase in K/S value as a result of melt blending ranged from 575.4 to 2860.5% indicating the enormous increase in disperse dyeability.

4.6. Fastness properties

Results in Table 6 indicate that the melt blend fibres exhibited very good washing and light fastness properties for all the dyeings obtained using different disperse dyes. PP:PTT :: 80:20 polyblend fibres showed slightly lower fastness properties, due to increase in the amorphous content of polyblend fibre structure which maybe causing some amount of desorption of the dye.

5. Conclusion

The foregoing discussion indicates that, PP/PTT blend fibres show very good promise for obtaining easy disperse dyeable polypropylene based melt blend fibres. Although the dyeability increased in many folds with increase in PTT content in the polyblend fibre, due to decrease in crystallinity and over all orientation, the tenacity of the blend fibres consequently decreased. Hence depending upon extent of dyeability and tenacity needed, proper selection of PP/PTT blend can be made.

Internal structural studies support the fact that it is the decrease in crystallinity and overall orientation, as a result of increase in PTT content in the polymer blend fibres which enabled this immiscible blend fibres to exhibit enhanced dyeability.

6. References

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