

## Imparting Disperse and Cationic Dyeability to Polypropylene through Melt Blending

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**Abstract:** The present paper deals with improvement in disperse dyeability as well as imparting of cationic dyeability to difficultly dyeable polypropylene by a melt blending technique. Isotactic polypropylene (PP) was blended with fibre grade polybutylene terephthalate (PBT), cationic dyeable polyethylene terephthalate (CDPET) and polystyrene (PS), individually. The resulting binary blends were spun and drawn into fibres at draw ratio 2, 2.5, and 3. The compatibility of blends, structural changes of fibres in terms of X-ray crystallinity, relative crystallinity, sonic modulus, birefringence and thermal stability were examined. The blended fibres were found to be disperse dyeable by the conventional method of high temperature and high pressure dyeing. And this dyeability increased with increase in the level of substitution. PP/CDPET blend also exhibited dyeability with cationic dyes in addition to that with disperse dyes. The optimum level of blending was predicted keeping in view of tenacity and thermal stability of melt blend fibres. The wash fastness properties of the dyed fibres were found to be of high rate.

**Keywords:** Melt blending, Polymer alloys, Polybutylene terephthalate, Cationic dyeable polyester, Polystyrene

### Introduction

In order to obtain new materials with improved properties, blending of polymers prior to the spinning becomes a quite useful technique. Fibres formed by an intimate mixing of two or more polymers before delivery to the spinneret, are generally called polyblend or alloy fibres. The purpose of blending polymers is either to improve processability, or more often, to obtain materials suitable for specific needs by tailoring one or more properties with minimum sacrifice in other properties [1].

Polypropylene (PP) in its inherent form is very difficult to be dyed with disperse dyes as well as with any other ionic dyes because of its high order of crystallinity and hence many producers are left with a limited choice but to get this fibre in mass coloured form while it is melt spun. Such fibres have obvious disadvantages due to restrictions on variety of shades demanded by the end users.

Perhaps the most important of the heterogeneous blend systems are high-impact plastics such as nitrile rubber blended with polystyrene or styrene-acrylonitrile copolymers, and butyl or ethylene-propylene rubber blended with polypropylene. The most important homogeneous systems are combinations of polymeric plasticisers with polyvinyl chloride to aid in processing at low temperature without reducing the glass transition temperature ( $T_g$ ) of the vinyl polymer. Other desirable modifications in polymer properties that can be achieved by blending polymers include increase in stiffness, strength, dimensional stability, toughness, heat distortion, temperature and mechanical damping, reduced cost, flammability and modified electrical properties. According to Gin and Brydon [2] thermal shrinkage of PP fibres at 150 °C can be greatly reduced by blending a minor component of a liquid crystal polymer

into the PP fibre. This can be also improved with repeated drawing and annealing. It has been also reported that blending of polymeric fine powder of glycidyl methacrylate and divinyl butylenes is effective to make PP disperse dyeable [3].

In the present work, it was intended to increase the accessibility of the polypropylene fibre structure for disperse dye and also to render it cationic dyeable. In order to achieve this object, fibre grade polybutylene terephthalate (PBT), cationic dyeable polyethylene terephthalate (CDPET) and atactic polystyrene (PS) were used.

### Experimental

#### Materials

##### Polymer Chips

Following commercially available polymer chips were used.

- (1) Isotactic polypropylene: Kolene XF B1 (supplied by IPCL Vdodhara, India)
- (2) Polybutylene terephthalate: Arnite T06-200, Unfilled (supplied by Century Enka Plastics, India)
- (3) Cationic dyeable polyester (supplied by J. K. Synthetics, Kota, India)

##### Dyes Used

Sr. no.	Brand name	C.I. Number	Mole. wt.	Migration rate
1	Foron Navy Blue S-2GLI	C.I. Disperse Blue 79	639	2
2	Foron Blue SE-RI	C.I. Disperse Blue 183	473	1-2
3	Foron Orange E-RLI	C.I. Disperse Orange 25	323	4-5
4	Sandocryl Blue B-3G	C.I. Basic Blue 3		
5	Sandocryl Red BLH	C.I. Basic Red 22		

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### Blending of Polymer Chips

The polymer chips of the respective polymers were weighed accurately on a single pan electronic balance and subsequently they were tumble mixed with each other and then spun into fibres using a melt spinning machine having a proper premixing facility of the molten mass.

### Melt Spinning of Polymer Blend Filament Yarns

The melt spinning experiments were carried out on Laboratory Melt Spin Extruder from Extrusion System Ltd., UK. Polymer chips were fed into the hopper which was connected to the dehumidifier of Piovan DS-403 type. The temperature of dehumidifier was kept between 80 °C-120 °C and chips were dried for 24 hours to ensure that they were completely dried. Then dried chips were moved forward to electrically heated extruder zone I, II and III [4]. The temperature of the extruder zones was kept 25 °C-50 °C above the melting point of the chips. In the extruder zone, the chips melted to form a molten mass which then moved further to a metering pump and to die head zone I and II. 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 bottom, middle and top pair of rollers. The drawing was carried out between the bottom and middle pair of rollers at the required temperature. The ratio of the speed of the middle roller to that of the bottom pair of the rollers was the measure of the draw ratio, whereas the speed of the top pair of rollers was kept as that of the middle pair of rollers. The filaments were finally fed to the take up winder machine over the condenser arm wheel, which applied tension to the yarn and controlled the speed of the spindle, ensuring the formation of consistent package.

For a melt spinning, two polymers are usually dry blended in a granular form, and melted, then intensively mixed in an extruder and spun into fibre. In some cases, the polymers may be precompounded in an extruder to ensure intimate mixing and palletized. The pallets are then used to spin the fibre. In melt spinning of condensation polymers, it is reported

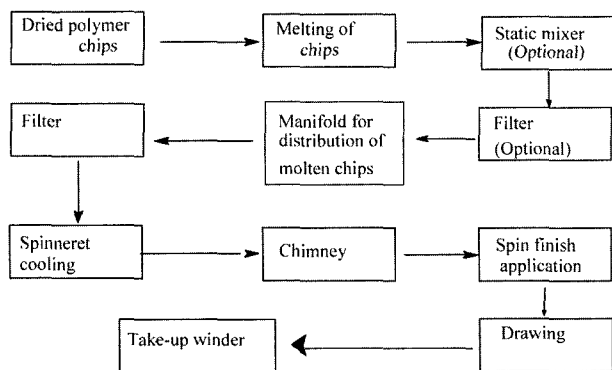


Figure 1. Flow chart of melt spinning process.

that certain interchain reactions, such as trans amidation, trans esterification and transesterification, may also occur [5,6].

### Analysis of Polymer Blends

Tenacity and elongation at break, X-ray diffraction analysis [7], crystal size, measurement of birefringence [8], sonic modulus [9], differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were carried out using standard techniques [10,11].

### Scouring

The yarn samples used for the dyeing were pre-scoured with 2 g/l of a nonionic detergent at 70 °C for 30 mins and subsequently rinsed with hot and cold water and then dried in air.

### Dyeing

Commercial samples of disperse and cationic dyes were used for the dyeing. The disperse and cationic dyeings of the prescoured fibres were carried out in a high temperature/high pressure beaker dyeing machine supplied by Parekh Engg. Co. Pvt. Ltd. India, using a standard method of the dyeing of synthetic fibres.

### Evaluation of Dye Uptake

The amounts of disperse dye as well as cationic dye present on the dyed fibre were determined by using Pye-Unicam SP B-400 UV-Vis spectrophotometer.

### Evaluation of Wash Fastness

The fibre samples were tested for relevant wash fastness using ISO-IV test in case of disperse and cationic dyes [12].

## Results and Discussion

### Compatibility

Results in Table 1 with respect to DSC and DTA analysis clearly indicate that there are two distinct melting points for PP/PBT blend. In case of pure polypropylene, the melting peaks were 171.35 °C and 169.0 °C on DSC and DTA, respectively. The other peak corresponded to PBT varied in the range of 224 °C to 226 °C for both analyses. This clearly indicates that PP/PBT blend is immiscible or an incompatible blend. The slight but distinct decrease or depression in the melting point of polypropylene in the PP/PBT blend was observed as the extent of a minor component (PBT) in the blend increased from 5 to 15 %.

Results from the Tables 2 and 3 for the blends of PP/CDPET and PP/PS indicated that these were also an immiscible or an incompatible blend having two distinct melting peaks corresponding to PP and CDPET in the blend. However, in case of PP/PS blend, there was a single melting peak observed as against the earlier two blends, indicating thereby PP/PS blend to be a miscible or compatible blend.

**Table 1.** Relative properties of PP/PBT blends

Properties	Blend composition, PP:PBT			
	100:0	95:5	90:10	85:15
DSC melting peaks, temp. °C	1) 171.35 2) –	168.22 224.28	167.17 224.30	165.97 224.38
DTA melting peaks, temp. °C	1) 169.00 2) –	169.00 226.00	169.00 226.00	169.00 226.00
X-ray crystallinity %	61.22	58.25	52.44	51.73
Crystal size, Å				
D(110)	73.770	80.274	84.155	85.248
D(040)	54.866	60.765	64.009	65.217
D(130)	63.846	60.822	59.581	58.225
Relative crystallinity	100.00	96.02	93.32	91.60
Birefringence, DR-3	0.05148	0.04870	0.04362	0.03871
Sonic modulus, DR-2	57.78	52.62	51.75	49.98
DR-3	74.05	69.41	67.33	66.25

**Table 2.** Relative properties of PP/CDPET blends

Properties	Blend composition, PP:CDPET				
	100:0	95:5	90:10	80:20	70:30
DSC melting peaks, temp. °C	1) 171.35 2) –	171.16 252.15	171.27 252.20	171.11 252.17	172.07 252.20
DTA melting peaks, temp. °C	1) 169.00 2) –	169.00 258.00	169.00 258.00	169.00 258.00	169.00 258.00
X-ray crystallinity %	61.22	60.37	58.23	57.82	56.23
Crystal size, Å					
D(110)	73.770	73.527	73.023	72.712	71.394
D(040)	54.866	55.275	58.372	60.158	63.295
D(130)	63.846	62.928	61.231	60.724	59.289
Relative crystallinity	100.00	95.84	92.18	89.50	88.35
Birefringence, DR-3	0.05148	0.04241	0.04038	0.03442	0.03091
Sonic modulus, DR-2	57.78				51.62
DR-3	74.05	73.84	64.79	64.85	63.01

**Table 3.** Relative properties of PP/PS blends

Properties	Blend composition, PP:PS			
	100:0	97.5:2.5	95:5	92.5:7.5
DSC melting peaks, temp. °C	175.60	172.18	171.96	168.90
DTA melting peaks, temp. °C	169	169	169	169
X-ray crystallinity %	65.73	57.56	56.53	51.11
Crystal size, Å				
D(110)	85.284	81.057	73.706	90.178
D(040)	57.372	43.249	51.355	82.290
D(130)	58.254	51.769	48.756	75.462
Relative crystallinity	100	98.42	97.44	96.62
Birefringence, DR-3	0.05532	0.05046	0.04025	0.03230
Sonic modulus, DR-4	75.72	69.25	68.07	65.82

### Crystallinity

X-ray crystallinity as well as the relative crystallinity values in case of PP/PBT, PP/CDPET and PP/PS blends decreased as the extent of substitution of PP by PBT, CDPET or PS increased. When PP was substituted by 15 % PBT, the X-ray crystallinity value decreased from 61.22 to 51.73 % and relative crystallinity value reduced from 100 to 91.60 %. When PP was substituted by 30 % of CDPET, the crystallinity value was found to be decreased from 61.22 to 56.23 % or relative crystallinity showed the decrease from 100 to 88.35 %. In case of PP/PS blend, the crystallinity decreased from 65.73 to 51.11 % or relative crystallinity decreased from 100 to 96.62 % as the amount of substitution of PP by PS increased to 7.5 %.

In other words, using a melt blend technique PBT, CDPET or PS which were intended to have lower crystallinity compared to PP, due to the presence of an aromatic ring in the polymer, the crystallinity of the blended polymer decreased significantly. This contributed enhancement in dye uptake as discussed further.

### Birefringence

The data from Tables 1 to 3 indicated, the progressive decrease in birefringence values as the PP was successively replaced with increase in quantity of PBT, CDPET or PS in the blend. It is obvious that PBT, CDPET and PS contain aromatic groups and hence this aromatic structure would bring down the orientation of the chain molecules. In addition, pendant Na salt of 5-sulpho isophthalic acid units in the CDPET and pendant phenyl rings in the PS polymers would be responsible for such a decrease in orientation as discussed further.

### Sonic Modulus

Data from Tables 1, 2 and 3 indicate that the sonic modulus values were maximum for pure PP and as PP was partially substituted by PBT, CDPET or PS in the blended polymers, the respective sonic modulus values decreased steadily. It is to be noted that lower draw ratio (2) gave lower value of sonic modulus compared to that of the higher draw ratio (3). The draw ratio having a positive influence on birefringence further confirmed its contribution towards overall orientation and it was for this reason, the tenacity was found to be increased.

### Thermal Stability

Figure 2 representing TGA curves for PP/PBT polymer blended fibres, showed that up to about 320 °C, degradation was minimum and upto 380 °C it was quite slow and beyond that temperature upto 400 °C it was quite rapid. However, still the degradation was confined to only 20 % weight loss where as beyond 400 °C, there was a rapid and drastic degradation. In general, in the earlier slower zone of degradation temperature upto about 380 °C, the addition of PBT seemed to have been imparting more and more thermal stability mainly

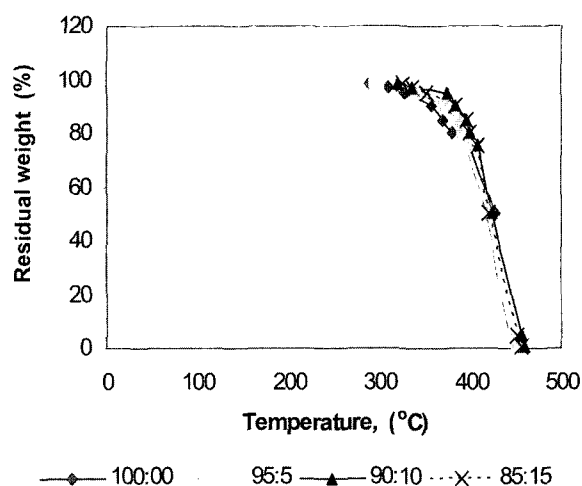


Figure 2. Thermogravimetric analysis of PP/PBT blend fibres (DR-3).

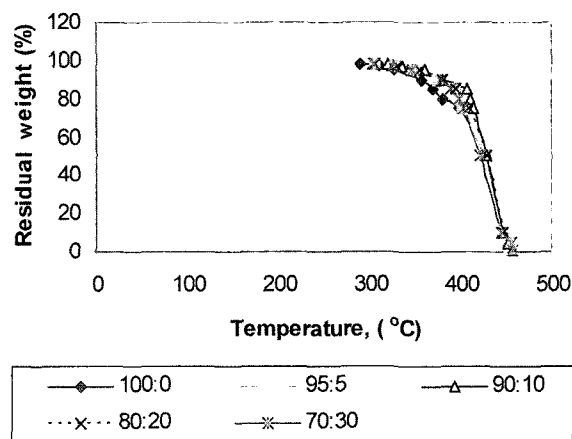


Figure 3. Thermogravimetric analysis of PP/CDPET blend fibres (DR-3).

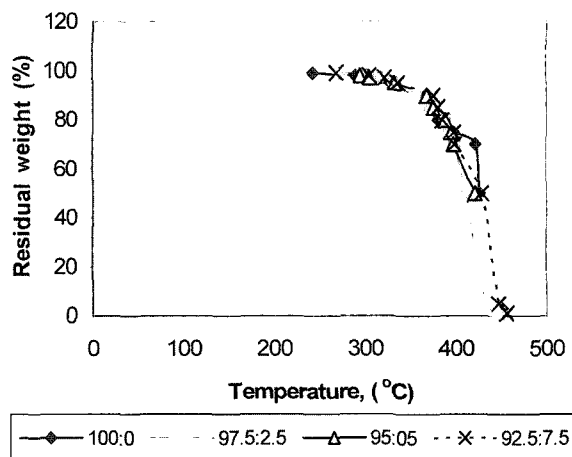


Figure 4. Thermogravimetric analysis of PP/PS blend fibres (DR-4).

because of the aromatic ring structure. Similar conclusions could also be drawn in case of PP/CDPET and PP/PS blended fibres (refer Figures 3 and 4). In other words practically the degradation of such blended fibres seemed to be taking place at much higher temperature than that of the processing temperature and hence they could be safely used for the apparel purposes, as discussed further.

#### Denier, Tenacity and Elongation at Break

Results in Tables 4 and 5 indicate that with increase in draw ratio, the denier of the melt blended yarn was found to be decreasing which is quite obvious due to increase in the orientation of the chain molecules, and compactness resulting

**Table 4.** Physical properties of the filament yarns obtained from PP/PBT blends

Blend composition (PP: PBT)	Draw ratio	Denier of 24 filament yarn	Tenacity (gms/denier)	Elongation at break %
100:0	2.0	176.4	1.957	213.35
	2.5	124.2	2.373	131.20
	3.0	121.5	2.762	125.35
95:5	2.0	166.5	1.892	252.75
	2.5	117.0	2.311	140.56
	3.0	110.7	2.712	112.31
90:10	2.0	144.9	1.823	192.69
	2.5	123.3	2.301	127.17
	3.0	113.4	2.584	99.54
85:15	2.0	171.9	1.302	133.66
	2.5	126.0	2.139	100.96
	3.0	110.7	2.524	76.28

**Table 5.** Physical properties of the filament yarns obtained from PP/CDPET blends

Blend composition (PP: PBT)	Draw ratio	Denier of 24 filament yarn	Tenacity (gms/denier)	Elongation at break %
100:0	2.0	176.4	2.106	213.35
	2.5	124.2	2.388	131.20
	3.0	121.5	2.762	125.35
95:5	2.0	155.7	2.066	225.73
	2.5	121.5	2.373	173.84
	3.0	117.9	2.671	148.90
90:10	2.0	157.5	2.025	216.00
	2.5	130.5	2.227	150.85
	3.0	115.2	2.641	121.62
80:20	2.0	160.2	1.944	242.37
	2.5	140.4	1.960	137.00
	3.0	107.1	1.976	119.70
70:30	2.0	166.5	1.211	161.00
	2.5	162.0	1.340	141.92
	3.0	137.7	1.371	115.17

out of it.

The tenacity of the yarn also increased with decreasing denier as a result of increased drawing. This is understandable due to increase in the orientation of the chain molecules which would also result in the increase in crystallinity. However the tenacity of the pure PP was found to be maximum. As the content of PBT or CDPET in the polymer blend increased substituting PP, the tenacity was found to be decreasing. Such a decrease could be attributed to decrease in the crystallinity as the PBT or CDPET content in the blend increased.

In case of PP/PS blends, as shown in Table 6, addition of PS in PP upto 5 %, the reduction in tenacity of spun blended fibres was tolerable; but substitution of 7.5 % PP by PS reduced the tenacity of spun fibre dramatically. As far as elongation at break was concerned, it was found to be the least for the fibres drawn at highest draw ratio of 3 and was maximum for the fibres drawn at the least draw ratio of 2.

#### Dyeability

For the dyeing of these melt blended fibres with some

**Table 6.** Physical properties of the filament yarns obtained from PP/PS blends

Blend composition (PP: PS)	Draw ratio	Denier of 24 filament yarn	Tenacity (gms/denier)	Elongation at break %
100:0	2.5	108.0	2.859	183.30
	3.0	88.5	3.547	151.23
	4.0	89.7	4.327	92.51
97.5:2.5	2.5	109.0	2.587	184.58
	3.0	88.7	3.101	178.70
	4.0	87.7	3.953	84.90
95:5	2.5	104.6	2.338	166.67
	3.0	86.1	3.096	148.68
	4.0	89.3	3.286	83.29
92.5:7.5	2.5	103.5	2.270	189.22
	3.0	87.0	2.341	139.11
	4.0	90.0	2.709	81.23

**Table 7.** Effect of blend composition of PP/PBT on disperse dyeability at DR-3

Dyes	Dye uptake, gm/kg of fibres			
	Blend composition, PP:CDPET			
	100:0	95:5	90:10	05:15
Foron Orange E-RLI	0.40 (0.55)*	0.90 (0.20)*	1.55 (2.00)*	2.00 (2.35)*
Foron Blue SE-2RI	0.10 (0.35)*	1.75 (2.10)*	3.40 (5.00)*	4.90 (7.45)*
Foron Navy Blue S-2GLI	0.35 (0.50)*	2.40 (3.00)*	3.40 (3.70)*	3.60 (4.00)*

(\*) DR=2.

**Table 8.** Effect of blend composition of PP/CDPET on disperse dyeability at DR-3

Dyes	Dye uptake, gm/kg of fibres				
	Blend composition, PP:CDPET				
	100:0	95:5	90:10	80:20	70:30
Foron Orange E-RLI	0.40 (0.55)*	1.25 (1.40)*	2.00 (2.30)*	3.10 (3.65)*	3.25 (3.70)*
Foron Blue SE-2RI	0.10 (0.35)*	2.20 (2.90)*	4.10 (5.30)*	7.30 (7.85)*	8.00 (8.85)*
Foron Navy Blue S-2GLI	0.35 (0.50)*	2.90 (3.20)*	3.15 (3.50)*	3.70 (3.90)*	3.95 (4.20)*

(\*) DR=2.

**Table 9.** Effect of blend composition of PP/PS on disperse dyeability at DR-4 (at 130°C & 2 % shade)

Dyes	Dye uptake, gm/kg of fibres			
	Blend composition, PP:CDPET			
	100:0	97.5:2.5	95:5	92.5:7.5
Foron Orange E-RLI	0.40 (0.55)*	0.55 (0.85)*	0.85 (1.30)*	1.10 (1.50)*
Foron Blue SE-2RI	0.10 (0.25)*	1.45 (1.850)*	2.30 (3.80)*	3.25 (4.2)*
Foron Navy Blue S-2GLI	0.05 (0.20)*	0.90 (1.30)*	1.70 (1.90)*	2.30 (2.85)*

(\*) DR=2.5.

**Table 10.** Effect of blend composition of PP/CDPET on disperse dyeability at DR-3 (at 130°C & 2 % shade)

Dyes	Dye uptake, gm/kg of fibres				
	Blend composition, PP:CDPET				
	100:0	95:5	90:10	80:20	70:30
Sandocryl Blue B-3G	0.00 (0.00)*	0.10 (0.20)*	0.14 (0.23)*	0.19 (0.29)*	0.40 (0.55)*
Sandocryl Red BLH	0.00 (0.00)*	0.15 (0.30)*	0.16 (0.35)*	0.20 (0.40)*	0.30 (0.45)*

(\*) DR=2.

disperse dyes, such as Foron Orange E-RLI, Foron Blue S-2GLI, Foron Navy Blue S-2GLI, low energy, medium energy and high energy dyes, respectively, the results obtained in terms of dyeuptake values are given in Tables 7-10. These results indicated that the dyeuptake values for fibres spun at draw ratio 3 were obviously lower than those for the respective fibres spun at draw ratio 2. While pure PP gave the least dyeuptake irrespective of the type of dye, as it was increasingly substituted either by PBT, CDPET or PS in polymer blend, the dye uptake was found to be progressively increased. This is understandable as the crystallinity and orientation were found to be decreased with increasing amount of PBT, CDPET or PS in the blend. Although the trend of dyeing remained

almost same for all the blends as well as pure PP, the absolute values of the dyeuptake varied depending upon the type of the dye used.

In case of cationic dye uptake of PP/CDPET blended fibres as shown in Table 10, although dyeuptake level was quite low, satisfactory dyeability leading to a brilliantly cationic dyed blended fibres was obtained. With increase in content of CDPET in PP/CDPET blend, dyeings were found to be more intense.

### Wash Fastness

The wash fastness of blended fibres for the dyeing with Foron Blue S-2GLI exhibited the wash fastness rate of 4-5 and 5, respectively, with ISO-IV washing test method. Similar results were observed in the case of dyeing with cationic dyes of PP/CDPET blended fibres.

### Conclusion

Good degree of disperse dyeability in case of PP/PBT and PP/PS blended fibres and disperse as well as cationic dyeability in case of PP/CDPET blended fibres was observed. From tenacity retention point of view, PP can be substituted upto 15 % by PBT, up to 10 % by CDPET and up to 7.5 % by PS in their respective blends. Adhering to above level of substitution, difficultly dyeable PP could be blended either with PBT, CDPET or PS to have improved dyeability with satisfactory level of fastness properties.

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