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Low temperature dyeing of PET / PTT blend fibers

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ABSTRACT

Polyester and Poly trimethylene terephthalate chips were melt blended in the ratio of 90/10, 80/20 and 70/30 and melt spun to make filaments. The compatibility of the fibre blends was proved by Differential Scanning Calorimetry study. The blend fibre showed decrease in glass transition temperature as well as melting point and also crystallization temperature. The melt blended fibres dyed with high energy disperse dyes gave the optimum dyeing depth for at 110° C as against 130° C required for normal polyester fibres. Also the depth of dyeing in case of melt blend fibre was significantly higher as compared to that observed in case of dyeing of virgin Polyester. The wash and light fastness of the dyed samples was also found to be same as observed in case of dyed virgin Polyester fibre. There was only marginal decrease in tensile strength of melt blend fibres.

Keywords: blend dyeing, disperse dyes, glass transition temperature, melt blend fibres

INTRODUCTION

Poly (trimethylene terephthalate) (PTT) a semi crystalline and aromatic polyester has been recently introduced as a commercial polymer, joining the other linear aromatic polyesters such as polyethylene terephthalate (PET) and poly butylene terephthalate (PBT). PET and PBT have been widely used as fibres, bottles, packages, etc because of its crystalline structure with satisfactory thermal stability and mechanical properties [1]. PTT is made by the polycondensation of 1, 3-propanediol (*PDO*) and terephthalic acid (TPA). Due to the different number of methylene group along the backbone of these polyesters, the chain flexibility of PTT is higher than that of PET, but lower than that of PBT. It enables to combine the desirable physical properties of PET i.e. strength, toughness, stiffness, and heat resistance with the processing advantages of PBT like low melt and mold temperatures, faster cycles and rapid crystallization, while retaining some basic benefits such as electrical insulation, dimensional stability, and chemical resistance. PTT can suitably be used in fibres, films, packing, and engineering thermoplastic markets because of these characteristics. [2]. PTT's soft hand, high stretch, and low disperse dyeing temperature are some of the advantages of PTT, over PET [3-5].

PTT has the property of fast crystallization and elasticity which makes it a well-liked candidate for Bi Component Filament (BCF) carpet yarn. BCF yarn made of PTT exhibits excellent bulk resistance and appearance retention along with good elastic recovery and strain resilience. Presently most applications make use of PTTs high elasticity in leisure and sportswear. Textiles that are made of PTT fibres have the properties of common fibres, such as spandex, nylon, acrylic and PET. The potential to replace the expensive high elastic polyurethane fibres lies in the properties like high stretch, bulk and softness [6]., PTT fibres and fabrics are disperse dyed at atmospheric boil without the need of a carrier as it has a low Tg [7]. PTT when dyed at atmospheric boil has very good colour fastness against light, ozone and NOx, similar to PET [8].

One of the effective techniques to develop new materials is polymer blending. It can develop materials with properties better than those of the original polymers. Blends of PET and PBT have been studied widely because of their commercial importance [9-16].PET is a slow crystallizing material [15] but PTT can crystallize easily without

the presence of any nucleating agent[16]. Therefore, blending of PET and PTT will offer an interesting way to combine the complementary properties of both the polymers. PET/PTT blends are fully miscible in amorphous state with criteria of microscopy morphology and thermal transition [17-18].

Jeon et al. [19] found the tensile strength and tensile modulus of PTT/PET blends and revealed that further introduction of PET to PTT will increase them further.

This piece of work will describe the study in which blends of PET and PTT would be spun by taking different ratios i.e. 90/10, 80/20 and 70/30 of PET/PTT and also 100% PET. The PET and its blends would then be dyed at four different temperatures to find out the optimum temperature required for dyeing two high energy disperse dyes. The miscibility of the blend will be investigated by DSC and structure –property relationship will then be explained.

MATERIALS AND METHODS

2.1 Materials

Commercial grades of polymers, dyes, chemicals and auxiliaries were used in the present study. Polyester (PET) chips having IV 0.73 was supplied by Reliance Industries Ltd., Mumbai and LLDPE having Melt Flow Index of 55 was supplied by Clariant Chemicals (India) Limited. PTT of IV 0.93 was obtained from Futura Polyesters, Chennai.

2.2 Chemicals

Commercial grades of polymers, dyes, chemicals and auxiliaries were used in the present study. Disperse Yellow Brown K2RS (C I Disperse orange 30) and Disperse Navy Blue 2GLS (C I Disperse Blue 79) were supplied by Color Band Ltd., Mumbai.

3. Experimental Methods

Melt Spinning

In order to remove traces of moisture the PTT chips were dried at 130° C for 4 hrs. The PET chips were dried in a vacuum dryer for 16 hrs at 150° C before melt spinning

The melt spinning of PET chips and its blend with PTT was carried out on Laboratory Melt Spinning M/c procured from Fair Deal Associates, New Delhi, India. Both the chips were tumble mixed just prior to spinning.

The different temperatures of the extruder zones maintained were 270°C, 285°C and 290°C for Zone-I, Zone-II and Zone III, respectively, and they were above the melting point of the PET chips. In the extruder zone Nitrogen gas can be supplied to prevent oxidation of PET. The molten mass of the melted chips moves to metering pump and further to die head zone. Blowing cool air in 1.5 meter long quench duct helps in cooling the filaments extruded from the spinnerets. These filaments were then guided to the godet roller via metered spin finish passage and then they were taken over to the draw rollers. Drawing was carried out by two stage drawing method at draw ratio of 3 which was previously optimized. The filaments were then fed to the take up winder machine where tension was applied on to the yarn and speed of the spindles is controlled in order to produce consistent packages. The final speed of melt spinning was 107 m/min and denier per filament was 8.

4. Characterization of Composite Fibers

4.1 Dyeing of Blend Fibers

From the package spun filaments were taken, cut into fine fibers then mixed thoroughly and dyed at four different temperatures i.e. 100, 110, 120 and 130^oC in high temperature / high pressure (HTHP) beaker dyeing machine with Disperse Yellow Brown K2RS, for 1% shade and Disperse Navy Blue 2GLS, for 3% shade. Both these dyes are high energy disperse dyes. These dyes were chosen as they require higher temperature to get exhaust on the PET.

Later the dyed samples were subjected for reduction clearing treatment for 20 minutes at 70° C with 2 gm/litre of caustic soda and 2 gm/litre sodium hydrosulphite. The fiber samples were washed at room temperature followed by neutralization with 1 gm/litre acetic acid solution ad were finally washed in water and air dried.

4.2 Evaluation of Colour Strength

The Color Depth evaluation of samples in terms of Kubelka Munk function (K/S) was done using a Spectra Flash® SF 300, Computer Color Matching System supplied by Data color International, U.S.A [20-21]. Kubelka Munk K/S function is given by:

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

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Where,

"K" is the absorption coefficient,

"S" is the scattering coefficient.

"R" is the reflectance at complete opacity,

4.3 Evaluation of Wash Fastness

The wash fastness of dyed samples was conducted as per ISO 3 in a Launder-O-meter for 20 minutes at 60 °C, using 2 g/l non-ionic soap (Auxipon NP) and 2 g/l soda ash at a liquor ratio of 50:1[20-21].

4.4 Evaluation of Light Fastness

Light Fastness was determined as per ISO 105-A02. Dyed fiber samples were stuck on a cardboard paper and its half portion of it was covered by a black sheet and remaining portion was exposed to light continuously for 17 hours. After that the fading of exposed samples was compared with Blue Wool Standards, which were also exposed simultaneously.

4.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (Shimadzu, Japan) was used to analyse the thermal properties of nano composites in a nitrogen atmosphere (flow rate 20ml/min) by [22]. All the samples were first heated at 290° C for 5 min and then quenched to 50° C in order to remove previous thermal history. The heating and cooling rates were set at 20° C/min. The second scanning of heating and cooling was then performed under the same conditions and the values are reported.

4.6 Tensile Strength and Elongation at Break

Tinius Olsen' M/c supplied by Aimil Ltd was used to measure the tensile strength and elongation at break of PET filaments. A single filament of test length 10 cm was used at an extension rate 50mm/min. Testing was carried out as per the test method ISO 5079 for breaking strength of fiber [23].

RESULTS AND DISCUSSION

5.1 DSC

Table I: DSC Data of PET/PTT blends

Sr. No.	Nature of Sample	Tg (⁰ C)	Tc Peak(⁰ C)	T _m Peak(⁰ C)	$\Delta H_{f}(J/g)$
1	PET 100%	76	194	251	37.12
2	PET/PTT (90/10)	73	178	247	33.28
3	PET/PTT (80/20)	70	167	238	26.77
4	PET/PTT (70/30)	65	160	231	23.34

 $Tg = glass transition temperature; Tc = crystallization temperature; T_m = Melting temperature; \Delta H_f = heat of fusion$

Fig.1: DSC Scan of PET and Its blends (a) 100% PET (b) PET/PTT (90/10) (c) PET/PTT (80/20) (d) PET/PTT (70/30)





Results from **Table I** and **Figs. 1 (a - d)** show a single Tg that depended on the composition of the blends in all the cases. This indicates that all the blends are compatible or miscible blends which may be attributed to the both polymer being polyester only. The Tg values of pure PET and PTT are 74 and 46° C respectively [24]. With the increase of PTT content in the blend the Tg values of the blends shift to lower temperature s from 73° C for 10% PTT to 65° C for 30% PTT. This is the result of the ester-interchange reaction of PET/PTT blends leading to the increase in homogeneity of the melt blends [24]. Thus the miscibility of PET/PTT blends is established.

The miscibility of the PET/PTT blends in the amorphous phase can also be seen in cold crystallization. A single and composition dependent Tc value can be observed for each sample In **Fig. 1** (**b-d**).

In the PET/PTT blends the polymer chains of PET and PTT are intimately mixed on fine molecular and segmental scales as indicated by the single composition-dependent Tg and T_{C} . These two intimately mixed chains act as a single chain segment with a single Tg in response to external thermal changes. They also respond simultaneously to temperature changes in concerted ways and reorganize simultaneously which resulted in a single T_{C} . All these features suggest that the miscibility of the PET/PTT blends is in the amorphous state[25].

With the addition of PTT the Tc of blends decreases nearly linearly which is low Tg component. The composition dependent behaviour of Tc in the blend can also be taken as a valid supportive evidence for miscibility as reported earlier [26].

5.2 Melting behaviour

An important feature of DSC Scan is the presence of a single melting point in each of the blends studied. (Fig. 1 {bd}). As the PTT content was increased the Tm of each component in the blends decreased. Similar melting point depression phenomenon has been reported in other binary crystalline polymer blends, such as PBSU/PEO, PBT/Par (I-100), PET/PBT etc [27-29]. For blends that are miscible, the melting point of the crystalline component is generally lowered with respect to the pure polymer, as a result of thermodynamically favourable interaction [30]. Therefore the melting point depression is used to evaluate the miscibility of polymer blends [31].

Noture of Somula	Duoing Tomporature (⁰ C)	V/S	$9/1$ memory in $K/S = 100^{9}$ C)	Colour co-ordinates		
Nature of Sample	Dyeing Temperature, (C)	к/б	78 merease in K/S w.i.t. 100 C)		a	b [*]
PET 100%		15.12	-	47.33	34.65	44.60
PET/PTT (90/10)	100	15.5	-	48.04	35.45	45.77
PET/PTT (80/20)	100	16.74	-	46.31	35.80	43.05
PET/PTT (70/30)	1 [18.79	-	45.91	37.18	42.35
PET 100%		16.31	7.85	48.66	38.28	46.93
PET/PTT (90/10)	110	17.96	15.84	46.39	35.82	43.27
PET/PTT (80/20)		20.4	21.83	45.80	37.69	42.52
PET/PTT (70/30)		23.81	26.71	47.02	36.58	44.30
PET 100%		19.69	30.19	47.77	38.51	45.71
PET/PTT (90/10)	120	17.86	15.2	46.05	36.18	42.93
PET/PTT (80/20)	120	20.07	19.84	45.56	37.27	42.41
PET/PTT (70/30)		23.41	24.59	45.12	38.65	41.81
PET 100%	130	24.26	60.43	46.48	37.86	43.72
PET/PTT (90/10)		17.57	13.31	46.33	38.57	43.65
PET/PTT (80/20)		18.88	12.73	45.69	40.22	42.66
PET/PTT (70/30)		20.95	11.49	44.94	36.92	41.24

Dye Used: Disperse Yellow Brown K2RS, Amax. abs.: 440nm Shade Dyed: 1%

Different PET/PTT blends were dyed at different dyeing temperatures with Disperse Yellow Brown K2RS, for 1% shade and Disperse Navy blue 2GLS for 3% shade and the results are given in **Tables II & III**.

It can be seen that as the temperature of dyeing increases from 100° C to 130° C, there is a progressive increase in depth of shade for PET fibre which is well known. But in case of PET/PTT blend as the temperature is increased from 100° C to 110° C the depth of the colour also increased. However at 120° C and 130° C, the depth of dyeing of respective samples with increasing temperature of dyeing was found to have been decreased. Also as the content of PTT component in the blend increased the depth of shade also became deeper.

	Duoing		% Increase in	Colour co-ordinates		
Nature of Sample	Temperature, (⁰ C)	K/S	K/S w.r.t. 100 ⁰ C)	L	a [*]	\mathbf{b}^{*}
PET 100%	100	23.93	-	17.62	2.00	-13.35
PET/PTT (90/10)		24.75	-	17.48	1.37	-11.99
PET/PTT (80/20)	100	25.24	-	16.68	1.51	-9.26
PET/PTT (70/30)		26.69	-	17.33	1.39	-11.43
PET 100%	110	26.65	11.36	15.95	1.70	-6.50
PET/PTT (90/10)		27.76	12.17	16.28	1.16	-7.35
PET/PTT (80/20)		30.1	19.25	16.10	0.86	-5.94
PET/PTT (70/30)		32.19	20.57	15.91	0.94	-5.35
PET 100%		29.21	22.06	15.73	1.04	-4.48
PET/PTT (90/10)	120	27.68	11.84	15.88	1.05	-5.28
PET/PTT (80/20)	120	29.85	18.27	15.70	0.83	-4.23
PET/PTT (70/30)		30.4	13.89	15.81	0.55	-3.74
PET 100%	130	32.52	35.88	15.92	0.78	-4.73
PET/PTT (90/10)		26.2	5.85	16.18	0.51	-5.32
PET/PTT (80/20)		27.63	9.46	15.79	0.64	-4.00
PET/PTT (70/30)		28.37	6.27	15.55	0.45	-2.50

TABLE III: K/S Values and Colour	Co-ordinates of Dyed P	ET/PTT blend fibres
Dye Used: Disperse Navy Blue 2GLS,	λmax. abs.: 600 nm	Shade Dyed: 3%

 TABLE IV: Wash, Light and Sublimation fastness of Dyed PET/PTT blend fibres

 Dye Used: Disperse Yellow Brown K2RS,
 λmax. abs.: 440nm
 Shade Dyed: 1%

Nature of Sample	Dyeing Temperature, (⁰ C)	Wash Fastness	Light Fastness	Sublimation Fastness		
				150°C	180°C	210°C
PET 100%	130	5	7	5	5	4
PET/PTT (90/10)	110	5	7	5	5	4
PET/PTT (80/20)	110	5	7	5	5	4
PET/PTT (70/30)	110	5	7	5	5	4

 TABLE V: Wash, Light and Sublimation fastness of Dyed PET/PTT blend fibres

 Dye Used: Disperse Navy Blue 2GLS,
 \lambda max. abs.: 600 nm
 Shade Dyed: 3%

Noture of Somple	Dyeing Wash		Light	Sublimation Fastness		
Nature of Sample	Temperature, (⁰ C)	Fastness	Fastness	150°C	180°C	210°C
PET 100%	130	5	7	5	5	4
PET/PTT (90/10)	110	5	7	5	5	4
PET/PTT (80/20)	110	5	7	5	5	4
PET/PTT (70/30)	110	5	7	5	5	4

In case of Disperse Navy Blue 2GLS, for 3% shade (**Table III**) the maximum depth of dyeing observed at 110° C and then reversal in trend was observed. The reason for this trend while dyeing blends of PET and PTT is quite obvious as the *T*g of the blends is less than the pure PET sample. The PTT also having lower *T*g, possesses the lower dyeing temperature and thus their multiple blends are expected to dye at lower temperature. Hence when higher temperature of dyeing than required is used e.g. 130° C, there is likelihood of dye getting diffused out in the bath resulting in lowering of shade.

The L, a* and b* values of the dyeings of blends did not show any significant changes when compared against that of 100% PET, indicating no significant tonal variation in the shade. The wash, light and sublimation fastness of the dyed blend samples at 110° C given in **Tables IV and V** were also found to be same as observed in case of 130° C dyed virgin PET fibre.

Figs 2 & 3 show the increase in the K/S (%) values of dyeing at respective temperatures above the K/S values of those dyeing carried out at 100° C. As expected for polyester with increase in temperature there was sharp rise in K/S

values whereas for PET/PTT blend fibres the maximum K/S was observed at 110° C as compared to 120° C and 130° C. However any dyeing temperature studied, the influence of PTT was clear in enhancing the dye uptake.



5.4 Mechanical Properties

Results from **Table VI** show the tensile strength, Elongation at break and % Crystallanity for PET and its blend fibres.

The PET and PET/PTT blend fibres did not show any appreciable change which is also reflected by almost no change in crystallinity. However the tensile strength and elongation (%) have been decreased marginally.

Nature of Sample	Tensile Strength (MPa X 10 ⁻²)	% Decrease in Tensile Strength	Elongation at Break (%)	% Crystallanity from XRD
PET 100%	5.29		82.60	22.12
PET/PTT (90/10)	5.19	1.89	79.40	23.42
PET/PTT (80/20)	5.13	3.02	78.00	23.57
PET/PTT (70/30)	5.00	5.48	74.00	23.63

Table VI: Tensile Strength and Elongation of PET and PET/PTT blend

CONCLUSION

Polyester (PET) and Poly (trimethylene terephthalate) (PTT) chips were melt blended compatibly and spun to make filaments. The blend fibres not only showed decrease in Tg, but also decrease in melting point and also crystallization temperature. When the aliphatic chain length in the fibre structure is increased, its Tg is decreased. The melt blended fibres when dyed with high energy disperse dyes; the optimum dyeing depth for the blended fibres was obtained at 110° C as against 130° C required for normal PET fibres as a result of the suppression in the glass transition temperature (Tg) of the PET due to the presence of PTT in the blend which has got lower Tg. Also the depth of dyeing in case of melt blend fibre was significantly higher as compared to that observed in case of dyeing of virgin PET. The fastness of the dyed samples was also found to be equivalent as observed in case of dyed virgin PET fibre accompanied by marginal decrease in tensile strength of fibres.

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