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Comparison of the Properties of False Twist Textured Super Bright, Semi-dull, Grey and Black Dope Dyed Polyethylene Terephthalate Yarns

Abstract
Dope-dyed polyethylene terephthalate (PET) set yarns, which are usually used for the production of fabrics dedicated to manufacture car seats, have better light and washing fastnesses when compared with those dyed with conventional methods such as carrier or high temperature dyeing. It is the aim of this paper to compare the properties of false twist-textured super bright, semi-dull, grey and black dope-dyed PET yarns including titanium dioxideand black pigments, respectively. X-ray diffraction (XRD) and DSC showed that the above mentioned additives lead to a rather looser microstructure. The loose structure exerted less resistance against the torsional and bending forces acting during the heat-setting of twisted yarn in texturing. The highest degree of crystalinity was observed for the super bright yarn. Titanium dioxide and black pigments led to an increase in the coefficient of friction of the false twist textured yarns. As a result of the additives, bulk and stretch ability of the textured PET yarn improved and its twist liveliness increased. Both the effects of additives on the fine structure as well as the coefficient of friction were held responsible for the differences seen as a result of dispersing titanium dioxide and black pigments in PET.

Key words: *PET yarns, false twist texturing, super bright, semi-dull, dope dyed PET, fine structure, physical properties, crimp properties.*

Introduction

Polyethylene terephethalate (PET), commonly known as polyester has become the raw material of the most important and fastest growing fibre over the past 50 years, accounting for around 40% of the total fibre market and expected to grow at around 7% per annum [1]. PET fibres are produced by the melt spinning process and contains ester groups (-CO-O-) in its main molecular chain. Ester groups are a result of the reaction between bi-functional carboxylic acids and bi-functional alcohols [2]. The dyeing and printing of unmodified PET fibres is limited to only disperse dyes [3]. This is due to the fact that PET is not capable of undergoing reaction with anionic or cationic dyes, as well as being a hydrophobe fibre. Moreover, under normal dyeing conditions, the compact structure of PET makes the penetration of disperse dyes inside it very difficult. To dye PET fibres, special conditions such as high temperature (about 130 °C), 'dry heat' (190 - 220 °C), or using carrier in the dye bath are required [4]. It is also possible to obtain colorued PET fibres by incorporating dyes or pigments in the molten polymer and then extruding through the spinneret in the usual way. This technique, which is called dope dyeing, also referred to as spin dyeing or mass pigmentation, gives rise to very bright and strong colours with excellent fastness to wet treatments. The light fastness of mass dyed PET yarns is also reported to be superior when compared with conventional dyed ones, making this kind of fibre a very suitable choice for the production of yarns for carpets and car seat covering in the automotive industry [5]. The dyes or pigments must enjoy enough heat stability to withstand the temperature of molten polymer. At the same time, to obtain a homogeneous appearance, the pigments must have optimal particle size [5, 6]. Mass dyeing has the advantage of more efficient and economical fibre production, reduced energy consumption and less pollution problems [7]. The cost of colorant in conventional dyeing has been reported to be 100% higher than in the mass colouration technique [8]. On the other hand, mass pigmentation has the disadvantage of having low color flexibility. Mass dyed PET as well as polyamide are being produced in large scales [5]. About 70% of mass dyed PET filament and staple fibres are black [9].

Normal PET fibres enjoy a wide spectrum of end uses, both as staple or continuous filament yarn in apparel, home textiles as well as other applications such as car seat covering [10]. Deficiencies related to the lack of bulk in flat continuous filament yarns make them unsuitable for apparel or some home textiles. Hence, texturising is employed to impart a lofty and bulky character to them [11]. The two major texturising techniques employed for PET yarns are false-twist and air-jet. The false-twist technique sets helical coils in the filaments of the yarn with the help of a false-twist device, positioned after a heating and cooling zone in the texturing machine. This technique depends on the thermoplasticity of the yarn being textured. Air jet texturing, also called, cold-fluid texturing, does not depend on the thermoplasticity of the yarn and imparts bulk to flat continuous filament yarns by forcing loops out of it. This happens when the yarn, in an overfed state, meets the turbulent flow of air in the air-jet [12]. Although, different aspects of false twist textured PET and polyamide yarns have been the subject of many published papers in the past 35 years [12], and literature review shows numerous publications on the properties and fine structure of PET fibres, no information concerning the effects of pigments such as titanium dioxide and carbon black on the properties and texture ability of dope dyed PET yarns was available. Tavanai *et al*. [13] studied the nucleation effect of pigment dyes on the microstructure of mass-dyed bulked continuous filament (BCF) polypropylene.

The aim of this research is to compare the texture ability and some physical characteristics of the super bright, semi-dull, and dope- dyed (grey and black) stretch false- twist textured PET yarns.

Table1. *Specifications of the super bright and semi-dull chips.*

Type of chips	Super bright	Semi dull
Intrinsic viscosity	0.64	0.64
Melting point °C	255	258
-COOH content	45	35

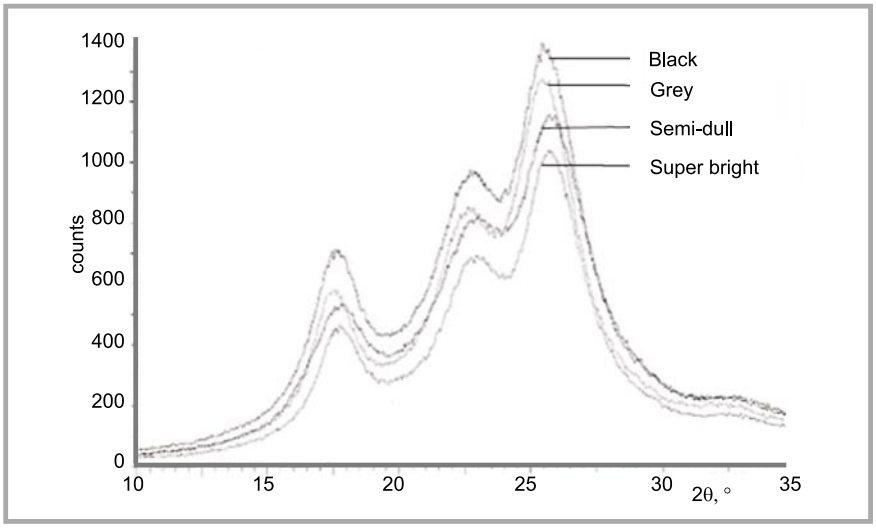

Figure 1. *Wide angle XRD patterns of false-twist textured polyethylene terephthalate yarns.*

Table 2. *Percentage crystalinity, crystalline order index and crystallite size in the (010) plane of the textured yarns (From XRD curves).*

Parameter	Super bright	Semi-dull	Grey	Black
Crystalinity index, %	71.1	66.9	70.9	66.2
Crystalline order index	1360	1210	1350	780
Crystallite size in (010) plane, A°	35.6 (Aş)	34.1 (Aş)	35.3 (Aş)	30.2 (Aş)

Experimental

Material

In this research four partially oriented PET yarns (POY) namely, super bright, semi-dull and dope- dyed (grey and black) with a linear density of 265 dtex and 48 filaments were used. These yarns were produced on a Noyvallensina (1979) melt spinning plant with a primary spinning speed of 3200 m/min. The semi-dull, grey and black yarns were produced from chips containing 0.4% titanium dioxide. The intrinsic viscosity, melting point and COOH content of super bright and semi-dull chips are shown in Table 1. As can be seen, there exist some differences in the melting point and COOH content of the chips, indicating a rather small difference in the polydispersity. Unfortunately, it was not possible to find super bright and semi-dull chips from one source with exactly the same properties. Throughout the paper, we will try to take this point into consideration when relevant. Dope- dyed grey and black yarns contained 0.65% and 2.25% of Estofil Black MP-NA masterbatch (Clariant), respectively. The finishing oil applied to the POY yarns was Dryfi 34M (Schill-Seilacher); and its amount was determined to be 0.35% of the fibre weight.

Sample production

To produce stretch textured yarn samples, the above-mentioned yarns were textured on the ICBT false-twist texturing machine (FTF12E2, 2001) with a speed of 650 m/min (second heater was turned off). The draw ratio and D/Y were 1.64 and 1.76, respectively. The false- twist aggregate had a configuration of 1-5-1. The active discs were polyurethane of 9 mm thickness and 52 mm diameter. The guide discs were of ceramic type. The primary heater temperature was 200 °C.

Methods

Wide angle X-ray diffraction patterns (WAXS) of yarns were obtained with the help of Philips X'pert with copper tube of wavelength 1.54 Å.

The coefficient of friction of the yarns was measured by HFT hairiness/friction tester (SDL) with a yarn speed of 100 m/min against aluminum. Five samples of 50 meter length were examined for each yarn.

Crystallisation and melting point of the yarns were measured by differential scanning calorimetry with DSC 2010 TA instruments.

The tenacity of the yarns was measured by a Zwick tensometer according to ASTM: D2256-80. 20 specimens were chosen for this test.

The bulk and stretch ability of the super bright, semi-dull, grey and black stretch yarns were measured according to DIN 53840. Five specimen were chosen for each yarn and the average of crimp contraction, crimp modulus as well as crimp stability values ware calculated.

The twist liveliness of the yarns was measured by the snarl test as follows:
A length of 1 metre of a tensioned yarn (0.11 cN/dtex) is measured. Then a load equivalent to 0.22 cN/dtex is suspended in the middle of the yarn. The two ends of the yarn are brought together slowly and allowed to snarl freely. The snarled yarn comes to rest after rotating forth and back. The number of turns in the snarl yarn, known as the snarl factor, is expressed as turns per metre and is taken as the twist liveliness of the yarn. In this case 5 tests were carried out for each yarn.

Results and discussion

Figure 1 shows the wide angle XRD diagrams of the yarns. Three fine structure related parameters, namely, crystallinity index, crystalline order index and crystallite size can be measured from the XRD curves [14]. Table 2 shows the results of these measurements. It is seen that the value of the three crystalinity related parameters decreases for the yarns in the order of super bright, grey, semi- dull, and black.

The lower values of crystallinity index, crystalline order index and crystallite size can indicate that the additives lead to a rather looser microstructure. It is reminded that one may expect that the higher polydispersity of super bright yarn lead to a rather looser structure and hence to a lower crystallinity related parameters. This highlights the effect of the additives such as titanium dioxide and black pigments on lowering the mentioned parameters and hence a looser structure. Looser structure leads to lower

Table 3. *Melting point (T_m), crystallization temperature (T_c), heat of melting (ΔH_m), heat of cooling (ΔH_c), heat of cold crystallization(ΔH_c^*) and percentage crystallinity of the textured yarns.*

Parameter, unit	Super bright	Semi-dull	Grey	Black
T_m, °C	253.2	254.8	253.5	252.4
T_c, °C	218	222.2	221.1	221
ΔH_m, J/g	64.0	59.2	57.0	61.9
ΔH_c, J/g	50.1	50.0	46.2	51.6
ΔH_c^*, J/g	0	0	0	0
Percentage crystalinity	45.6	42.2	40.6	44.2

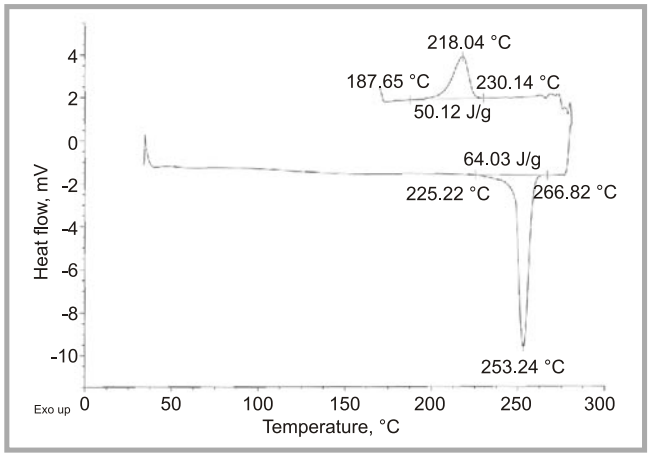

Figure 2. *DSC diagram for super bright false-twist textured polyethylene terephthalate yarn.*

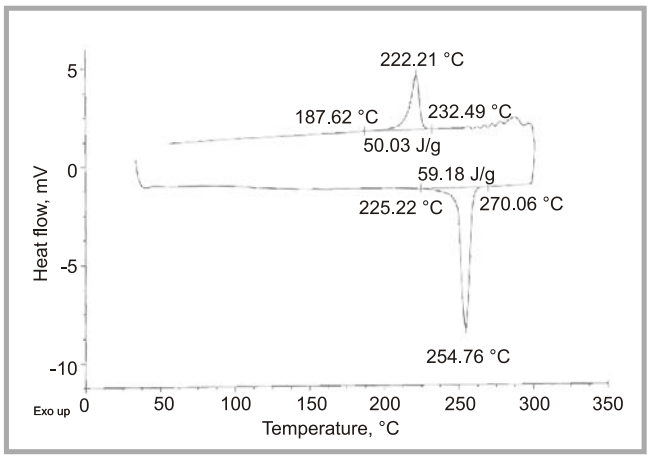

Figure 3*. DSC diagram of semi-dull false twist textured polyethylene terephthalate yarn.*

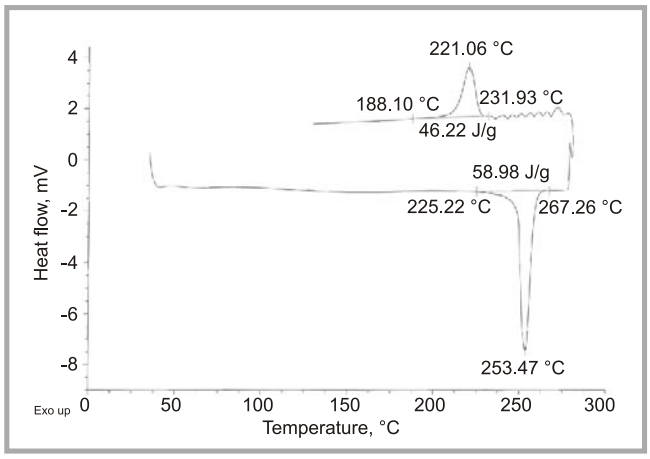

Figure 4. *DSC diagram of grey false-twist textured polyethylene terephthalate yarn.*

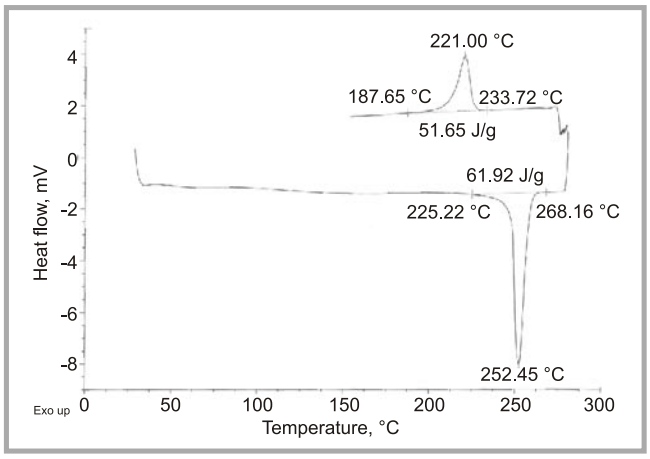

Figure 5. *DSC diagram of black false-twist textured polyethylene terephthalate yarn.*

resistance against the bending and torsional forces encountered by yarn during false- twist texturing. This conclusion is further strengthened by the results shown in Table 3 which was obtained from the DSC thermograms of the yarns shown in Figures 2, 3, 4 and 5. Melting point (T_m), crystallisation temperature (T_c), heat of melting and heat of cooling are the important information obtainable from DSC thermograms. Percentage crystallinity can also be obtained from DSC thermograms by the following formula:

$$\text{Percentage crystallinity} = \\ = 100\ \{[\Delta H_m - \Delta H_c^*] / \Delta H_m^0\}$$

ΔH_m, ΔH_c^* and ΔH_m^0 show the heat of melting, heat of cold crystallisation and reference value (heat of melting for 100% crystalline PET), respectively. The reference value for PET is 140.1 J/g [15]. As can be seen, the thermograms show no distinct T_g and heat of cold crystallisation. This is due to the heat treatment during the texturing process. Table 3 shows that T_m decreases from semi-dull to grey and black. As the lower polydispersity of the super bright chips may have contributed to a lower melting point for the super bright yarn, additives can be hold responsible for a looser structure of the yarns and a lower melting point as a result. T_c appears to be lowest for the super bright yarn by about 4 °C and the other three yarns show nearly the same T_c. Lower T_c indicates a rather longer time required for the melt, leaving the spinneret to crystallise and somehow a higher resistance against crystallisation. In other words, the presence of additives such as titanium dioxide and carbon black make crystallisation occur sooner than when they are not present. This could be related to their nucleation effect. As far as heat of melting is concerned, super bright yarn shows the highest value of 64 J/g and the other yarns vary with no particular trend between 57 and 61.9 J/g. Similar to the data in Table 2, super bright yarn shows the highest percentage of crystall-inity. However, it must be pointed out that the crystallinity percentage values measured from DSC thermograms are lower than the crystallinity index measured from

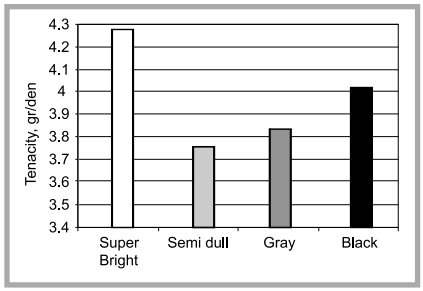

Figure 6. *Tenacity of the false-twist textured PET yarns.*

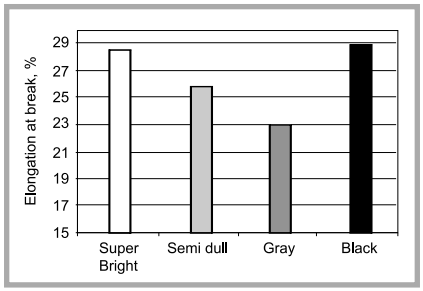

Figure 7. *Elongation at break of the false-twist textured PET yarns.*

Table 4. *Results of ANOVA for tenacity of super bright, semi-dull, grey and black textured yarns (Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (5.08%)	Semi-dull (7.31%)	Grey (4.68%)	Black (3.34%)
Super bright		+	+	+
Semi-dull	+		-	+
Grey	+	-		+
Black	+	+	+	

Table 5. *Results of ANOVA for elongation at break of super bright, semi-dull, grey and black textured yarns (Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (9.05%)	Semi dull (11.9%)	Grey (9.83%)	Black (6.12%)
Super bright		+	+	-
Semi-dull	+		+	+
Grey	+	+		+
Black	-	+	+	

Table 6. *Results of ANOVA for crimp contraction of super bright, semi-dull, grey and black textured yarns (Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (5.6%)	Semi dull (2.04%)	Grey (5.40%)	Black (2.30%)
Super bright		+	+	+
Semi-dull	+		-	-
Grey	+	-		-
Black	+	-	-	

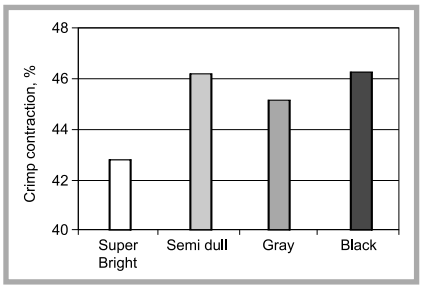

Figure 8. *Crimp contraction of the false-twist textured PETyarns.*

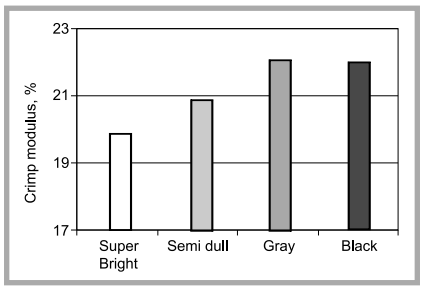

Figure 9. *Crimp modulus of the false-twist textured PET yarns.*

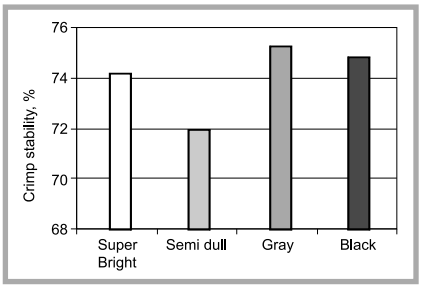

Figure 10. *Crimp stability of the false-twist textured PET yarns.*

XRD patterns by an average of about 25%. At the same time, the trend of crystallinity index for the semi-dull, grey and black is not exactly the same for XRD and DSC measurements. On the whole, the super bright yarn shows the lowest T_c, highest ΔH_m and highest degree of crystallinity.

Figures 6 and 7 compare the tenacity and elongation at break of the textured yarns respectively. The results of ANOVA for tenacity and elongation at break of the yarns are shown in Table 4 and 5 respectively. It is seen that super bright yarn shows the highest tenacity. For the other three yarns, tenacity increases in the order of semi- dull, grey and black. As Table 5 shows, the difference between super bright and black is not significant at 95% level. As far as the relationship between crystallinity index, crystalline order index and crystallite size is concerned, it can be said that for super bright, semi-dull and grey yarns, there exists a direct relationship between tenacity and the mentioned parameters. However, the black yarns do not follow this pattern. It is interesting to note that the trend of the tenacity variation of the yarns agrees somehow with the percentage crystallinities obtained from DSC diagrams (Table 3). Attention is drawn to the fact that according to Figure 6, the maximum difference between the tenacities of the semi-dull, grey and black yarns is in the order of about 0.2 g/dtex, and it may not be possible to expect an exact trend between the tenacity and the crystallinity related parameters obtained from XRD patterns. As far as elongation at break is concerned, there exists a very good agreement between it and the XRD parameters. In fact, extension at break increases as the XRD parameters decrease.

On the whole, it can be said that titanium dioxide and black pigments may leave some negative effect on the tenacity and elongation at break.

Figures 8, 9 and 10 compare the crimp contraction, crimp modulus and crimp stability of the textured yarns, respectively. It is seen that super bright yarn shows the lowest crimp contraction and crimp modulus. Tables 6, 7 and 8 show the result of the analysis of variance for crimp contraction, crimp modulus and crimp stability respectively at 95% significance level. Analysis of variance showed that only the difference between the crimp contraction of super bright and the other three yarns was significant, but the difference between the crimp contraction

Table 7. *Results of ANOVA for crimp modulus of super bright, semi-dull, grey and black textured yarns(Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (11.6%)	Semi dull (2.79%)	Grey (3.26)	Black (3.01%)
Super bright		-	+	+
Semi-dull	-		+	+
Grey	+	+		-
Black	+	+	-	

Table 8. *Results of ANOVA for crimp stability of super bright, semi-dull, grey and black textured yarns (Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (9.00%)	Semi dull (4.22%)	Grey (2.70%)	Black (7.25%)
Super bright		-	-	-
Semi-dull	-		-	-
Grey	-	-		-
Black	-	-	-	

Table 9. *Results of ANOVA for twist liveliness of super bright, semi-dull, grey and black textured yarns (Percentages in brackets show the coefficient of the variation); + significant at 95% level, - not significant at 95% level.*

Yarn type	Super bright (7.05%)	Semi dull (7.85%)	Grey (5.83%)	Black (8.13%)
Super bright		+	+	+
Semi-dull	+		-	-
Grey	+	-		-
Black	+	-	-	

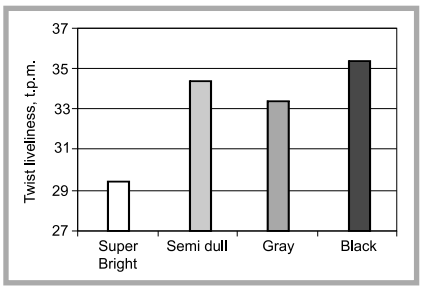

Figure 11. *Twist liveliness of the false-twist textured PET.*

Table 10. *Coefficient of friction of the textured yarns; (Percentages in brackets show the coefficient of the variation).*

Textured PET yarn (200 °C)	Coefficient of friction
Super bright	0.31 (3.97%)
Semi-dull	0.33 (3.71%)
Grey	0.33 (2.00%)
Black	0.33 (1.20%)

of semi-dull, grey and black yarns was not significant. Analysis of variance also shows that the crimp modulus of the super bright yarns is significantly different from grey and black yarns but not different from semi-dull. Also semi-dull yarns is different from grey and black yarns, but grey and black yarns are not significantly different. It may be concluded that crimp modulus shows practically the same trend as crimp contraction, i.e. semi- dull, grey and black yarns show the same crimp modulus. As far as crimp stability is concerned, ANOVA shows no significant difference between all the yarns. It is concluded that, assuming the same intrinsic properties for super bright and semi- dull chips, super bright yarn shows a considerably higher resistance against the structural changes brought about by the false-twist texturing process. Although as already metioned, it is expected that the higher polydispersity of super bright chips lead to a rather looser structure and hence less resistance against deformation and as a result, better texture ability. This strengthens the conclusion that semi-dull and dope-dyed yarns have a better texture ability than the super bright and additives such as titanium dioxide and black pigments lead to a better bulk and stretch ability for the textured PET yarns. As already concluded, this positive effect is due to a looser fine structure brought about by the addition of the mentioned additives.

Figure 11 compares the twist liveliness of the yarns. As it is seen, super bright yarn shows the lowest twist liveliness. Moreover, twist liveliness shows the same trend as crimp contraction and crimp modulus. This is expected as both crimp contraction and twist liveliness increase with increasing twist up to a certain extent. The result of ANOVA for twist liveliness is shown in Table 9. ANOVA shows that only the super bright is different from the other three yarns at 95% significant level and there is no difference between the twist liveliness of semi-dull, grey and black yarns. Therefore, it is concluded that TiO_2 and black pigments lead to a higher twist liveliness. As already mentioned, the additives lead to a looser fine structure and hence a lower resistance against the changes during heat-setting i.e. better twist development or higher energy absorption, leading to a higher detorque required to open the twisted structure of the heat set yarn after the spindle. As a result, a higher twist liveliness or residual torque develops.

Table 10 shows the coefficient of friction of the yarns. As can be seen, the super bright yarn shows the lowest coefficient of friction (0.31) and the other three yarns have equal coefficients (0.33). This shows that titanium dioxide and black pigments increase the coefficient of friction of PET yarns. Hence, the lower bulk and stretch ability of super bright yarn may also suffer from its lower coefficient of friction, which leads to a lower torque generated by the interaction between the moving yarn and the rotating friction discs during texturing. In other words, titanium dioxide and black pigments can lead to a better texture ability via their higher coefficient of friction (It is reminded that the torque generated in false twist friction texturing depends on the coefficient of friction between the yarn and friction discs). Of course, as already mentioned, the fine structure, with its effect on the mechanical properties such as elastic modulus and torsional and bending rigidity, is another important element affecting the physical properties and texture ability of the yarns. To determine the contributions of fine structure and coefficient of friction on the properties of the textured yarns is interesting and may be the subject of further research.

Summary

XRD and DSC studies showed that super bright yarn had the highest degree of crystalinity. It is also concluded that the additives such as titanium dioxide and black pigment lead to a quite looser microstructure which in turn may lead to a lower tenacity. As far as crimp contraction and twist liveliness are concerned, the rather looser structure of dope-dyed as well as semi-dull yarns exerts less resistance against the torsional and bending forces acting during the heat- setting of twisted yarn in texturing and hence a better bulk and stretch ability result. Twist liveliness also increases as a result of the additives inside the polymer. The results also showed that titanium dioxide and black pigments increase the coefficient of friction of the yarns and the improvement in stretch ability is partly due to this increase in the co efficient of friction of the yarns.

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