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Preparation and Properties of Opaque Polyethylene Terephthalate/TiO_2 Filaments

Zhaolin LIU [1, 3, 4], Yang YANG [2], Yuwen WANG [4], Xuehui GAN [5], Ni WANG [4] *

[1] *College of Textile and Garment, Hebei University of Science and Technology, Shijiazhuang 050018, China*
[2] *The Institute of Equipment Technology, Academy of People's Armed Police, Beijing 100012, China*
[3] *Hebei Textile and Garment Technology Innovation Center, Shijiazhuang 050018, China*
[4] *Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China*
[5] *College of Mechanical Engineering, Donghua University, Shanghai 201620, China*

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The opaque polyethylene terephthalate (PET) filaments with 0 % to 9 % mass fractions of TiO_2 particles were prepared by low-speed melt spinning and drafting. Basic structures including surface morphology, linear density, orientation degree and crystallinity, and properties including tensile and optical property of the PET/TiO_2 filaments were systematically analyzed, especially the visual shielding property. The results showed that TiO_2 particles were well-distributed on the filament surface at 3 % TiO_2 mass fraction, whereas agglomeration of TiO_2 particles appeared when the mass fraction of TiO_2 reached to 6 % and 9 %. The addition of TiO_2 increased the linear density of the PET filaments. The orientation degree of the filaments was positively correlated with the drafting ratio but hardly influenced by the mass fraction of TiO_2. The crystallinities achieved the maximum of 60.72 % and 54.99 % at the draw ratios of 3.5 and 4.0 respectively when the mass fraction of TiO_2 was 3 %, and then decreased gradually to 38.5 % or 34.74 % at 9 % TiO_2 mass fraction. The tenacities of the filaments reduced to 20.41 % and 25.50 % with the increasing TiO_2 content at the draw ratios of 3.5 and 4.0 respectively. However, the elongation at break enhanced as the TiO_2 content changed from 0 % to 3 % and then decreased to 42.53 % and 27.22 % respectively at the draw ratios of 3.5 and 4.0 with the increasing TiO_2 content. The opaque effect of the PET filaments improved significantly when the mass fraction of TiO_2 was less than 6 %, whereas the improvement of the opaque effect slowed down as the mass fraction of TiO_2 increased further.
Keywords: PET filament, TiO_2, tensile property, visual shielding property.

1. INTRODUCTION

The aims for wearing clothes have expanded with the development of society and scientific technology, while for warmth and shielding are remaining the most primary and basic purposes the same as before. Up to now, research on the fabrication and shielding property of clothes is still very limited. Only the visual shielding characteristics of silk fabrics were concerned. Li et al. [1] discussed the defilade property of silk fabrics and found that the special structure made the crepe de Chine fabric have excellent visual shielding property. Based on the relationship between color elements (lightness, hue and purity) and visual shielding property of the fine silk fabrics, Jiang et al. [2] concluded that color cooperation of the terrace clothing had influence on the visual shielding property, which was the best if colors of the inner and outer clothing were of complementary hue. The continual thinning of yarn fineness results in the lack of visual shielding more and more serious. Therefore, it is necessary to take efficient measures to improve the visual shielding property of fabrics and maintain their light weight, color and comfortability simultaneously. It is worth noting that the visual shielding property could be affected by fibers, yarn or fabric structures, and finishing due to the complexity of textiles. However, structure change is difficult to meet high visual shielding requirement and finishing often deteriorates comfort of the fabrics. Thus, application of opaque fibers is considered to be the most feasible and effective approach to enhance visual shielding [3, 4].

It is known that the visual shielding property could be improved through the reduction of light transmittance by means of intensifying light absorption and scattering. Since the light absorption coefficient of a certain material is constant and particles with high absorption coefficient are usually not suitable for the preparation of opaque fibers, how to maximize light scattering by adding particles has become the key point to obtain opaque fibers [5]. According to Mie scattering theory, the relative refractive index of a particle is a fundamental parameter influencing the scattering power, besides the particle size, shape and surface roughness. Most of the opaque fibers are produced by adding high refractive index mineral fillers, such as TiO_2, amorphous silica and silicates, aluminum trihydrate and ZnO, among which TiO_2 is of particular attractiveness owing to its white color and high stability. Solbrig et al. [6] studied the physical and morphological change of PET yarns hydrolyzed with NaOH and containing four concentrations of TiO_2 delusterants as 0, 0.1 %, 0.3 % and 2.0 %, respectively. They found that all the PET yarns showed progressive weight loss with the increasing hydrolysis time. Yarn tenacity began to deteriorate but there was no change in crystallinity after 6 h of hydrolysis. Surface morphology of the yarns with TiO_2 differed from that without TiO_2 additive. Huang et al. [7] blended TiO_2

* Corresponding author. Tel.: +86-21-67792717; fax: +86-21-67792627.
E-mail address: *wangni@dhu.edu.cn* (N. Wang)

into PET fibers at different proportions to make semi-finished products by melt spinning. The structures of TiO_2 on fiber surface were explored by the scanning electron microscopy and energy dispersive X-ray spectroscopy. The results indicated that TiO_2 could be evenly distributed on the fiber surface. Zhu et al. [8] pointed out that PET integrated with TiO_2 nanoparticles could have a lower crystallization temperature and melting point compared with pure PET. The TiO_2 nanoparticles after surface treatment have relatively less influence on the PET lattice matrix. Han et al. [9] prepared PET/nano TiO_2 composite fibers by adding rutile TiO_2 into the system via in situ polymerization. It was found that rutile TiO_2 dispersed in the matrix uniformly when the mass fraction of TiO_2 was l %. Compared with pure PET fibers, PET/nano TiO_2 composite fibers exhibited lower breaking strength, lower elongation at break and crystalline. Furthermore, the fabrics had splendid screening effect against UVA and UVB with an ultraviolet protection factor above 50.

For the development of opaque PET filaments, the mass fraction of TiO_2 is much higher than that in the semi-dull or dull PET filaments [10]. However, there is little research related to the effect of high percentage TiO_2 on the structures and properties of opaque PET filaments, especially the visual shielding property. In this study, opaque PET filaments added with different mass fractions of TiO_2 particles were prepared by low-speed melt spinning and drafting. The basic structures including surface morphology, linear density, orientation and crystallity, and the properties including tensile and visual shielding of the opaque PET filaments were systematically investigated. Close attention was paid to the visual shielding property.

2. EXPERIMENTAL DETAILS

2.1. Materials

The materials used included fiber-grade PET chips with an intrinsic viscosity of 0.69 dL/g and high TiO_2 containing PET master batch, both of which were provided by Zhejiang Xinxin Chemical Fiber Co., Ltd. (China). TiO_2 particles were well dispersed in the PET matrix with a mass fraction of 50 % in the PET master batch.

2.2. Preparation of PET/TiO_2 filaments

PET chips and master batch were first pre-crystallized by DGG-9070 electric thermostat blast drying oven. The temperature began at 90 ℃ and increased by every 10 ℃ per hour until 120 ℃ for the maintenance of 2 h. The pre-crystallized chips were then dried at 155 ℃ for 48 h to make the moisture content lower than 50 ppm by JM-500ZGX dynamic vacuum dryer. The PET chips and master batch were blended in proportion to match the ratio listed in Table 1. Mass fractions of the added TiO_2 were 0, 3, 6, 9 %, respectively.

The undrawn yarns (UDY) were spun on ABE-25 spinning frame with a speed of 800 m/min. The obtained UDY were drawn on a TF-100 parallel-draft machine with the draw ratio0 of 3.5 and 4.0, respectively. Temperatures of the hot plate and hot disc were set as 80 ℃ and 160 ℃. Detailed parameters of the melting spinning process are given in Table 2. The resultant PET/TiO_2 filaments prepared with various TiO_2 mass fractions and different drawing ratios were denoted as TiO_2-x/DR-y.

Table 1. Mass fractions of PET and TiO_2 in the PET/TiO_2 filaments

Mass fraction of PET chips, %	Mass fraction of master batch, %	Mass fraction of TiO_2, %
100	0	0
94	6	3
88	12	6
82	18	9

2.3. Characterization

Morphologies of the PET/TiO_2 filaments were observed by JSM-5600LV scanning electron microscopy (SEM). The filaments were sputter-coated with a gold layer of 10 nm thickness before scanning and the acceleration voltage was 15 kV.

After humidity-adjustment under the standard condition of 65 % relative humidity and 20 ℃, the linear density of the PET filaments was calculated according to the relationship between weight and length. Orientation degree of the PET filaments was measured on SCY-III fiber sound velocimeter developed by Shanghai Donghua Ltd., China.X-ray diffraction (XRD) patterns were evaluated on the D/max-2550P X-ray diffractometer to calculate the crystallinity. The CuKa radiation with a wave length of 1.542 nm was generated at 40 kV and 200 mA. All the samples were scanned at the speed of 20 °/min in the 2θ ranging from 3 ° to 60 °.

Tensile properties of the filaments were tested using YG061 tensile test machine with a gauge length of 500 mm and a speed of 500 mm/min. The tenacity, initial modulus and elongation at break were obtained by calculating the average value of 30 trials for each sample.

The visual shielding effect of the opaque PET filaments was evaluated by Hitachi U-4100 Ultraviolet Visible Near-Infrared Spectrophotometer. The filaments were wrapped around a transparent glass slide in turn. Each filament was strictly controlled to wind 90 laps within the length of 3.5 cm and maintain uniform tension during the winding process. The scanning was ranged from 350 nm to 800 nm with a speed of 300 nm/min and a resolution of 2 nm. The transmission and reflection spectra of the PET filaments with various TiO_2 mass fractions were obtained.

Table 2. Melt spinning parameters of the PET/TiO_2 filaments

Samples	Screw extruder temperatures, ℃				Spin pump temperature, ℃	Bending tube temperature, ℃	Spin head temperature, ℃
	I	II	III	IV			
TiO_2-0, TiO_2-3, TiO_2-6, TiO_2-9	282	300	295	295	295	295	293

3. RESULTS AND DISCUSSION

3.1. Surface morphology

Fig. 1 shows the SEM images of the PET filament surfaces with 0 %, 3 %, 6 % and 9 % TiO_2 at the draw ratio of 3.5, where the gray areas and white dots represent the PET matrix and TiO_2 particles respectively. It can be seen that surface of the pure PET filament is smooth. TiO_2 particles are well dispersed on the filament surface without forming significant aggregation when the mass fraction of TiO_2 is 3 %. As the mass fraction of TiO_2 reaches to 6 % and 9 %, agglomeration of TiO_2 particles can be observed.

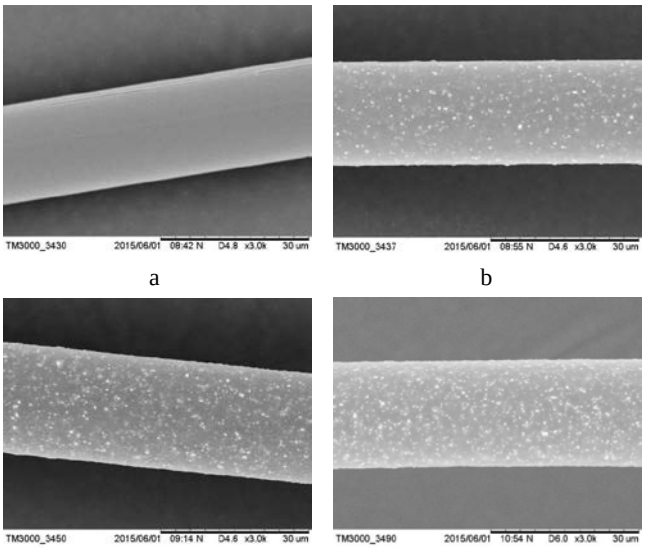

Fig. 1. SEM images of the PET filament surfaces at the draw ratio of 3.5 with different mass fractions of TiO_2: a – 0 % TiO_2; b – 3 % TiO_2; c – 6 % TiO_2; d – 9 % TiO_2

3.2. Linear density

Linear densities of the PET filaments are demonstrated in Fig. 2. Because the density of anatase TiO_2 is 3.8 – 3.9 g/cm^3, much larger than that of PET [11], therefore, the linear densities of the filaments with the addition of TiO_2 show an increasing tendency compared with pure PET filaments. On the other hand, the higher is the draw ratio, the smaller is the linear density.

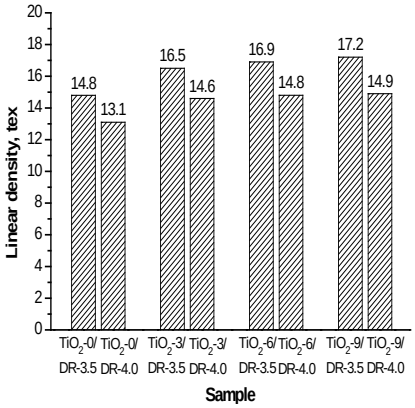

Fig. 2. Linear densities of the PET filaments with different mass fractions of TiO_2 and draw ratios

3.3. Orientation degree and crystallinity

The orientation factor of the PET filaments with different mass fractions of TiO_2 and draw ratios is listed in Table 3. It could be concluded that draw ratio has significant influence on the orientation degree of PET filament. The macromolecular chains are arranged in parallel along the direction of external force with the increasing draw ratio, thus the orientation factor of the macromolecular chains of the filaments becomes larger with the increase of draw ratio. However, there seems no obvious law between the orientation degree of the filaments and the mass fraction of TiO_2.

The XRD patterns of the PET filaments are given in Fig. 3. It can be seen clearly that new curves appear after the addition of TiO_2 at 2θ equals to 38°, 48°, 54° and 55°. Both the increase of TiO_2 mass fraction and the draw ratio have nothing to do with the position of the curves. Compared with the results of the standard PDF card of TiO_2, it can be concluded that the new curves come from the anatase type of TiO_2.

The calculated crystallinity of the PET filaments is listed in Table 3. No matter the draw ratios are 3.5 or 4.0, the crystallinity of the PET filaments enhances as the TiO_2 mass fraction changes from 0 % to 3 %, and then decreases as the TiO_2 mass fraction continues to augment. When a small amount of TiO_2 is added into the PET filaments, the TiO_2 particles act as the nucleating agent and PET molecules are inclined to form regular alignment of the crystalline region. As a result, the crystallinity shows a rising trend initially. However, when the TiO_2 content exceeds 6 %, the large amount of TiO_2 plays the role of cross-linking, making the PET molecular chains difficult to slip along external force and leading to the reduction of crystallinity.

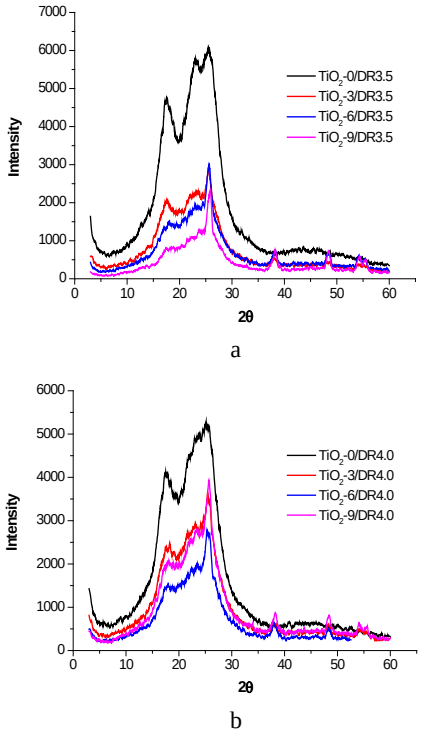

Fig. 3. XRD patterns of the PET filaments with different mass fractions of TiO_2 and draw ratios

Table 3. Orientation factor and crystallinity of the PET filaments with different mass fractions of TiO_2 and draw ratios

Sample	TiO_2-0/ DR-3.5	TiO_2-0/ DR-4.0	TiO_2-3/ DR-3.5	TiO_2-3/ DR-4.0	TiO_2-6/ DR-3.5	TiO_2-6/ DR-4.0	TiO_2-9/ DR-3.5	TiO_2-9/ DR-4.0
Orientation factor	0.7993	0.8911	0.8134	0.8864	0.8194	0.8864	0.8220	0.8653
Crystallinity, %	30.28	34.75	60.72	54.99	47.89	38.07	38.5	34.74

3.4. Tensile property

The tensile property of the PET filaments are displayed in Table 4. The tenacity shows a gradual declination with the increase of TiO_2 mass fraction, while the elongation at break has a nonlinear relationship with the TiO_2 content.

On one hand, the TiO_2 particles could reduce the interaction force between the PET macromolecular chains. On the other hand, the intensified TiO_2 aggregation at high TiO_2 mass fraction results in the deterioration of interfacial defects and the aggravation of stress concentration. That is why the tenacity of the PET filaments decreases with the growing TiO_2 content. Similar conclusions have been obtained from the study of PA6/POE-g-MAH/nano SiO_2 composites and PA66/Mica composites [12, 13].

The elongation at break of the PET filaments improves when the mass fraction of TiO_2 is 3 % and then reduces with the TiO_2 mass fraction, but the variation is rather slight overall. The initial increase of the elongation at break can be ascribed to the ball-like role playing by the small amount of TiO_2, which weakens the interaction force between PET molecular chains and makes the relative slip between molecular chains easy to produce. On the contrary, brittleness of the PET filaments would increase as the content of TiO_2 reaches 6 %, leading to the drop of the elongation at break. From the analysis above, in order to maintain necessary strength and toughness of the opaque PET filaments, the mass fraction of TiO_2 should be carefully regulated.

3.5. Visual shielding property

The transmission and reflection spectra of the PET filaments with different mass fractions of TiO_2 and draw ratios are shown in Fig. 4. It can be found that the light transmittance of the PET filaments diminishes while the light reflectance increases with the increasing mass fraction of TiO_2 at both the draw ratios of 3.5 and 4.0. Furthermore, the changes of light transmittance and light reflectance tend to be more obvious when the TiO_2 mass fraction ranges from 0 % to 3 % than those when the TiO_2 mass fraction is within 3 % to 9 %.

The transmittance of pure PET filaments is up to 73.6 % at the draw ratio of 3.5 but drops to below 40.6% when the TiO_2 mass fraction is 3 %. Similarly, the transmittance of pure PET filaments is as high as 68.7 % at the draw ratio of 4.0 and decreases to less than 37.7 % when the TiO_2 mass fraction is 3 %, meaning the overall opaque effect of the filaments is significantly enhanced after adding a tiny amount of TiO_2. The interface between PET molecular chains and TiO_2 enlarges as more TiO_2 particles are added, resulting in more light reflection and scattering.

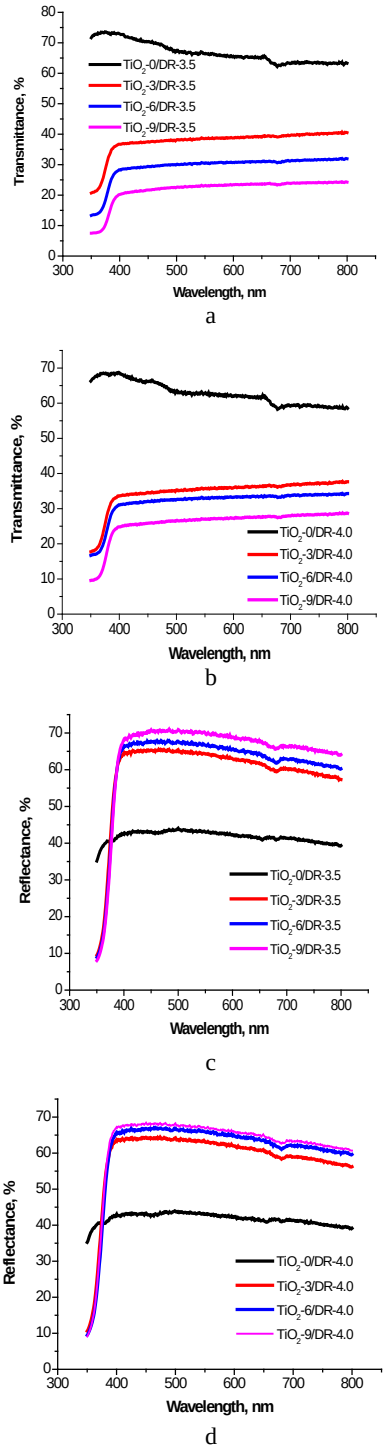

Fig. 4. Transmission and reflection spectra of the PET filaments with different mass fractions of TiO_2 and draw ratios

The path through which light is transmitted extends correspondingly, therefore, the transmittance of the PET filaments decreases with the increasing TiO_2 mass fraction.

The reflectance of the PET filaments increases significantly after the addition of TiO_2, since the refractive index of TiO_2 is much higher than that of PET. Similar result has been acquired when we studied the influence of TiO_2 on the optical property of PET films [14]. Both the decrease of light transmittance and the increase of light reflectance can improve the opaqueness of the PET filaments effectively.

Table 4. Tensile properties of the PET filaments with different mass fractions of TiO_2 and draw ratios

Sample	Tenacity, cN/tex	Elongation at break, %	CV of tenacity, %
TiO_2-0/DR-3.5	24.36	41.51	4.72
TiO_2-0/DR-4.0	30.78	28.63	1.97
TiO_2-3/DR-3.5	22.53	45.03	5.07
TiO_2-3/DR-4.0	26.60	29.47	3.78
TiO_2-6/DR-3.5	21.83	44.52	5.65
TiO_2-6/DR-4.0	25.59	28.24	4.21
TiO_2-9/DR-3.5	20.41	42.53	3.74
TiO_2-9/DR-4.0	25.50	27.22	3.21

4. CONCLUSIONS

The opaque PET filaments were prepared by melt spinning and drafting with the addition of TiO_2 particles. The structures and properties of the opaque PET filaments were systematically analyzed and the following conclusions can be drawn:

1. TiO_2 particles dispersed evenly on the surface of PET filaments when the mass fraction of TiO_2 was less than 3 %, and then TiO_2 agglomerated as the mass fraction of TiO_2 reached to 6 % and 9 %.
2. The orientation degree of the PET filaments was positively correlated with the draw ratio. However, the change of orientation degree was not obvious with the addition of TiO_2. The crystallinity achieved the peak value when TiO_2 mass fraction was 3 %, and then decreased as the TiO_2 mass fraction continued to grow.
3. The tenacity of the PET filaments showed a gradual declination with the increase of TiO_2 mass fraction. Whereas the elongation at break raised when the mass fraction of TiO_2 was 3 %, and then reduced with the addition of TiO_2.
4. The transmittance of the PET filaments decreased sharply and the reflectance of the PET filaments intensified as the content of TiO_2 was 3 %. Therefore, the opaque effect of the PET filaments improved significantly. When the content of TiO_2 ranged from 6 % to 9 %, the variation of the transmittance and reflectance tended to be slight, making the improvement of the opaque effect slow down.

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