Physical and Mechanical Properties of Nylon 6/ Titanium Dioxide Micro and Nano-Composite Multifilament Yarns

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ABSTRACT

In this study, the effect of titanium dioxide particles (TiO_2 micro and nano) on the physical and mechanical properties of Nylon 6-based multifilament yarns was investigated. For this reason, master-batches of Nylon 6/TiO_2 micro and nano-particles were prepared by melt compounding before spinning and then multifilament composites incorporating 0.03, 0.33, 0.5 and 0.7% TiO_2 micro and nano-particles were successfully spun in a melt-spinning machine.

Characterization of these composite multifilament yarns was carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive x-ray (EDX), and X-ray diffraction (XRD) analysis. Characterization of mechanical strength properties including tenacity and elongation at break of the resultant composites are discussed as a function of filler loading.

Through the application of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), it was found that incorporating micro titanium dioxide caused severe aggregation at the nylon fiber surface. By contrast, the diffusion of nano-particles within bulk of multifilament yarns was much more consistent, although aggregation of the titanium dioxide nano-particles still appeared. The results manifested the improvement of mechanical properties of the nano-composites containing TiO_2 nano-particles.

Keywords: Nylon 6, Multifilament Yarns, TiO_2, Micro and Nano-Particulates, Nano-composite, Physical properties, Mechanical properties.

INTRODUCTION

Among the other synthetic polymers, polyamide has been widely investigated as effective materials for textile and industrial applications for a long time.

Nylon 6 is frequently used because of its thermal stability and stiffness together with moderate cost, relatively easy processing, and good elastic recovery. However, the problem with these polymers is low heat distortion temperature and dimension instability. Studies have shown that dispersing inorganic particles such as titanium dioxide into the polymer matrix leads to dramatic property enhancement, such as increased mechanical properties, better dimensional stability, and surface appearance compared to unfilled polymer [1-6].

It seems that when the size of particles transmits from micro to nano, because of significantly increased interfacial interaction between inorganic and organic phases and size-dependent phenomena of nano-scale particles, polymer nano-composites are capable of markedly improving the properties compared to micro-composites [7, 8]. In addition, the improvements in properties of nano-composites are achieved at very low loadings of the nano-scale inorganic component (<5wt%), while traditional micro-composites usually require a much higher loading in the order of 25-40 wt% [9-12].

In order to characterize the properties of nano-composites comprehensively, not only describing the behavior of nano-composites under various conditions is enough, but also comparing the features of their performance with that neat polymer or the conventional filled composites is necessary [13-16].

Various approaches for the preparation of nano and micro-composite multifilament yarns of titanium dioxide have been reported, such as dip coating in solution, electrospinning, chemical vapor deposition, sol–gel technology, and melt spinning [17-23].

Introducing nano-particles of TiO_2 into commercial nylon fibers will turn them to multifunctional fibers.

This research focused on preparation of Nylon-6/ TiO$_2$ composite by the melt-spinning method. Producing nano and micro-composite fibers via melt spinning is a real challenge because enhancement in melt viscosity and particles agglomeration leads to filter blockage and fiber breakage during winding. In spite of some problems which occur in the melt spinning processes of synthetic nano-composite fibers, this method is a cost-efficient, highly productive, and environmentally friendly processes. The presence of TiO$_2$ particles inside polyamide matrix may increase the rate of photo-degradation (photo-tendering) of nylon at wavelengths above 300 nm [24-26]. Some materials may have side effects, but usually render another characteristic which somehow covers these side effects. Moreover it was assumed that using nanoparticles may decrease these side effects because of the decreasing the amount and size of the particles.

Nonexistence of a delustering agent in the body of synthetic fibers will lead to an undesirable glossy state [16]. Titanium Oxide is one the oldest and most conventional agents for this purpose. Besides, it shows other interesting properties such as self-cleaning, antibacterial, UV blocking substrate, catalytic, purification, and optoelectronic devices, especially in its nano scale [27-37].

To overcome the problems which occur in the melt spinning processes and have homogenous dispersion, nano and micro-particles were mixed with polymer granules before the extrusion process and then nano and micro-composite multifilament yarns were prepared by melt-spinning. The morphological structural characteristics of the fibers were investigated by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive x-ray spectrometry (EDX). Here, special attention was given to the effects of the size and concentration of particles on the mechanical properties of nylon micro and nano-composite yarns.

EXPERIMENTAL
Materials
In this research two experiments were conducted in parallel. One was the fabrication of Nylon 6/ TiO$_2$ micro-composite, while the other was the production of Nylon 6/ TiO$_2$ nano-composite. Nylon 6 granules were purchased from Aliaf Co., Iran which was considered as the matrix material in this study. The characteristics of Nylon 6 chips for fiber spinning were as follows; density: 1.12-1.15 g/cm^3, melting point: 220°C and relative viscosity: 2.20-2.32. Spherical titanium dioxide (TiO$_2$, P-25) nano-particles in the form of white powder (average particle diameter 21nm, specific surface area 50±15 m^2/g, density 3.8 g/cm^3) were obtained from Degussa Corporation, Germany. Nano-crystalline titanium dioxide was a mixture of anatase (80%) and rutile (20%) phases. Micro-TiO$_2$ with a mean size of 0.22 μm was a product from DuPont of the USA. All materials were used as received, without further purification.

Methods
Preparation of Micro and Nano-Composite Master-Batch
Before mixing, to secure a completely moisture-free state, powdered Nylon 6 and TiO$_2$ micro and nano-particles were dried in a vacuum oven at 90°C for at least two hours and then cooled to room temperature. The composite granules (master-batch) were prepared by mixing Nylon 6 powders with the titanium dioxide micro and nano-particles with desired compositions in a Twin Screw Extruder (DSE25-Brabender, Germany) which the rotor speed, and mixing temperature were 250 rpm and 250°C, respectively. After a defined period of time, the extruded material was cooled in a water bath, pelletized, and cut and chip master-batch obtained. To achieve a good dispersion, the master-batch was extruded under the same condition a second time.

Preparation of Micro and Nano Multifilament Composite
Prior to melt extrusion, both Nylon 6 pellets and the prepared Nylon 6/TiO$_2$ master-batches were dehumidified by using a vacuum oven for two hours at 100°C. The micro and nano-composite multifilament yarns were processed in a Twin screw extruder (Twin-Screw Extruder-Rhodia technology) with a rounded spinneret. The temperature profiles in the barrel were regulated between 260°C and 265°C from hopper to die. The extruded filament was cooled in a flow of ambient side-blown air in a quenching chamber to which no spin finish was applied. Samples were prepared in which the content of micro and nano titanium dioxide particles in the Nylon 6 matrix was set to 0.03, 0.33, 0.5 and 0.7wt%. For comparison purposes, fibers without particles were also spun under the same conditions. Fibers with a linear density of 0.56 Tex were obtained.

Characterization
Mechanical Properties
The tensile properties were determined with a tensile testing machine (Tinius Olsen-H5KT, America) according to ASTM D3822-95a. The gauge length and crosshead speed were 100 mm and 100 mm/min, respectively. Each result reported is the average of at least 10 measurements for each sample. The test was performed at room temperature.

Morphology Observation
To identify the titanium dioxide particle dispersion in the Nylon 6 matrix, the morphology of each sample was observed using a scanning electron microscope (SEM-XL30, Phillips-Holland) operating at 20 kV and employing magnifications of up to 30000. Before SEM observations, samples were coated with a thin layer of gold by a physical vapor deposition sputtering machine (Bal-Tec, Swiss) for 5 min to avoid electrostatic charging during inspection.

Transmission electron microscopy (TEM) imaging was performed on an EM 208-Philips to observe the morphology, distribution, and average particle size of TiO_2 in the polymer blends. Prior to the experiments, ultrathin sections (thickness: 100 nm) were obtained on a Reichert microtome (Ultracut OmU-3) with a diamond knife while no further staining was used to improve contrast. The TEM micrographs were taken at certain magnifications and all images were obtained under ambient conditions.

EDX Analysis
The elemental composition analysis of Nylon 6/TiO_2 micro and nano-composite was determined using an energy-dispersive X-ray spectrometer (EDX) attached to the scanning electron microscope. Gold layer was deposited on the samples before the analysis.

XRD Analysis
X-ray diffraction (XRD) analysis was carried out for identification of the TiO_2 crystal phase, and the structures of the micro and nano-composite fibers. XRD studies were carried out with an XRD Bruker-D8ADVANCE (Germany); x-ray Tube Anode: Cu; wavelength: 1.5406 Å (Cu Kα); filter: Ni. The diffraction peak angles (2θ) of each sample were measured from 3 to 70 at a scan speed of 0.05°/sec.

The crystallite size was calculated using Scherrer's equation [38]:

$$D= \frac{K \times \lambda \times 180}{\beta \times \pi \times \cos \theta} \tag{1}$$

Where λ is the wavelength of the incident X-ray beam (1.54056 for the Cu Kα), K is the shape factor which is often assigned a value of 0.89 if the shape is unknown, D is the average diameter of the crystals in angstroms, θ is the Bragg angle in degrees, and β is the full width at half-maximum of the strongest characteristic peak in radians.

RESULT AND DISCUSSION
Characteristics of the Surface
Scanning electron microscopy was used to observe the morphology and investigate the dispersion and distribution of titanium dioxide particles in the polymeric matrix. The SEM images of TiO_2 composite fibers containing micro and nano-particles are shown in *Figure 1*. The morphology of the fibers containing micro TiO_2 particles is illustrated in *Figure 1 (e, f, g and h)*. The structures of the fibers are rougher in comparison with nano-composite multifilament yarns shown in *Figure 1 (a, b, c and d)*. In addition, the nanoparticles in the fibers are more spherical in comparison with micro particles. It is also evident from the figure that the nano-composite multifilament yarns have a looser agglomeration structure compared to micro-composite ones and most of the nano- TiO_2 particles have an average diameter of ca. 60 nm in polymer matrix. There is severe aggregation of the micro-particles at the fiber surface because of attractive interaction forces between them [39-45].

The properties of composites can be normally controlled by the size and dispersion of the fillers in the polymer matrix which could have an influence on the mechanical properties and performance of composites. The particles size plays a primary role in determining their mixing and interface adhesion to the polymer matrix. It is reasonable to expect that the larger particles do not mix homogeneously, so they agglomerate easily and remain in the polymer surface, while the smaller particles will penetrate deeper and adhere strongly into the polymer [46-50].

Also agglomeration of particles may cause leakage in spinning process and necking phenomena which lead to yarn breakage. Moreover, the aggregation of TiO_2 particles in the polymer matrix increased with increasing TiO_2 content [16, 51-53].

Further, TEM was employed to investigate the morphology and dispersion of the Nylon 6 /TiO$_2$ nano-composites. *Figure 2* shows the TEM micrograph of Nylon 6/TiO$_2$which contain 0.7 wt% of nano TiO$_2$. It can be seen that the average diameters of the nearly spherical TiO$_2$ nanoparticles are ~60nm also the particles are quite well distributed in the polymer and less agglomerated.
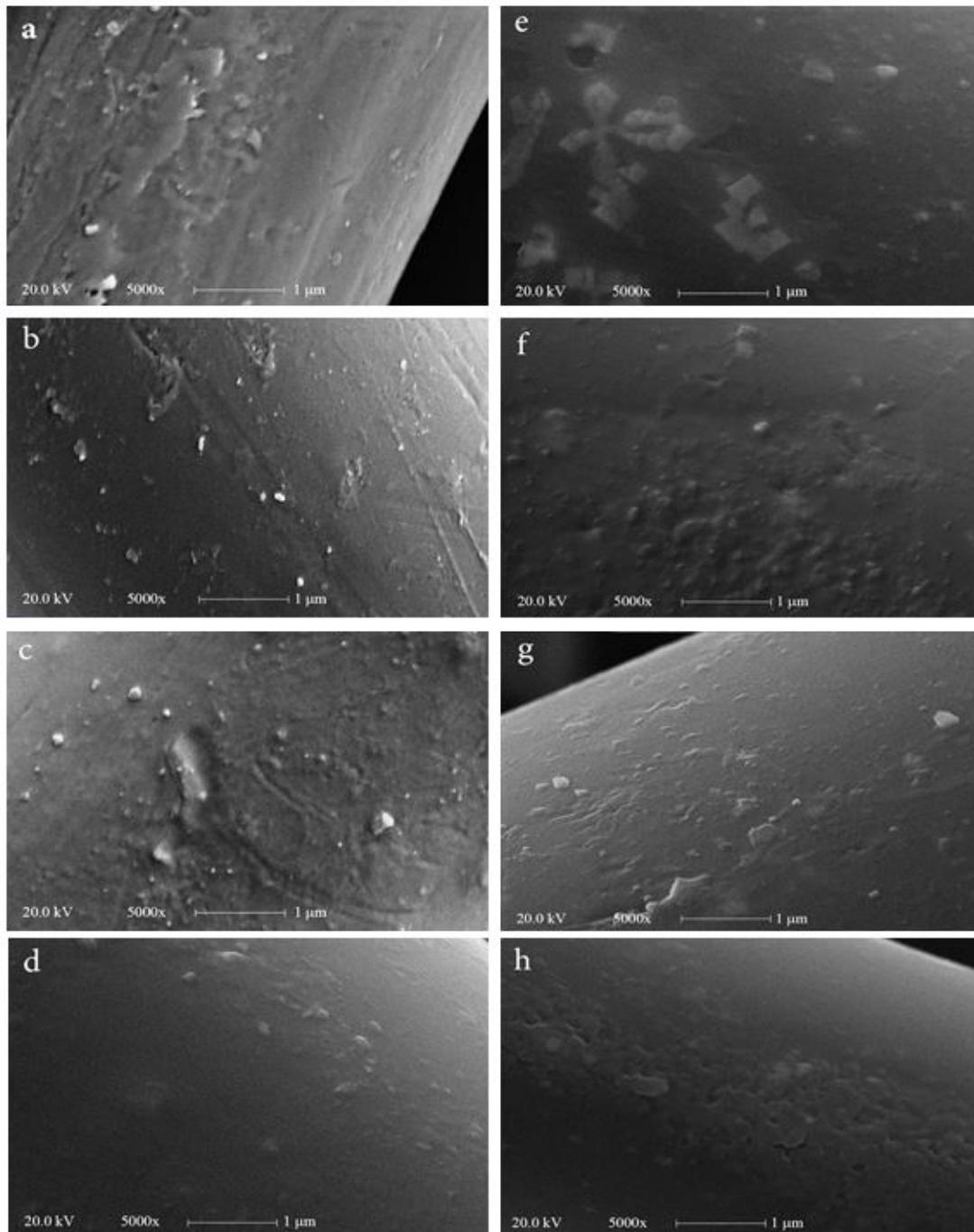

FIGURE 1. SEM micrographs of Nylon 6/TiO$_2$ composite (a) 0.03 wt% of nano TiO$_2$, (b) 0.33 wt% of nano TiO$_2$, (c) 0.5 wt% of nano TiO$_2$, (d) 0.7 wt% of nano TiO$_2$, (e) 0.03 wt% of micro TiO$_2$, (f) 0.33 wt% of micro TiO$_2$, (g) 0.5 wt% of micro TiO$_2$, (h) 0.7 wt% of micro TiO$_2$.
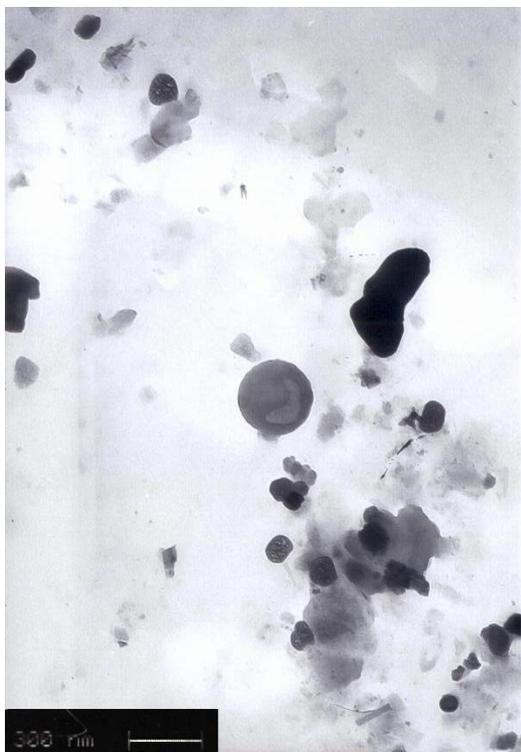
FIGURE 2. TEM micrographs of Nylon 6/TiO_2 nano-composite containing 0.7 wt% of nano TiO_2

Elemental Analysis

The titanium dioxide on the fiber surface was identified by energy dispersive x-ray (EDX) done during the SEM testing. The total TiO_2 content in the composites was calculated on the basis of measured Ti content. EDX pattern of the samples proved the existence of TiO_2 on the composite surface.

The results in *Figure 3* show the percentages of detected TiO_2 on the surface of composite and it confirms quantitatively that by increasing the amount of TiO_2 particles, the quantity of particles on the surface of composite increases. It is also evident that the amounts of micro TiO_2 is higher as compare to nano-particles which is in agreement with the SEM results that show most of the micro TiO_2 exists on the fiber surface.
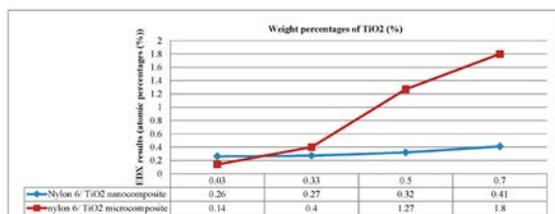

FIGURE 3. EDX results of Nylon 6/TiO_2 composite containing different amounts of TiO_2.

Structural Properties

The integrated XRD patterns of the micro and nano-composite fibers with different TiO_2 contents are illustrated in *Figure 4*.

Based on these patterns, TiO_2 particles consisting of anatase and rutile structure exist in all different multifilament composites. Major crystal peaks assigned to TiO_2 anatase phase according to the Joint Committee on Powder Diffraction Standards reference (JCPDS No. 21-1272) with trace rutile (JCPDS No. 21-1276) phase appeared. The results of *Figure 4* show that anatase peaks are sharp with high intensity ($2\theta = 25.2$) whereas rutile peaks are smaller ($2\theta = 27.44$). The results are shown in *Table I*.

Nylon 6 is known as a crystalline polymer. According to the Joint Committee on Powder Diffraction Standards reference (JCPDF No. 43-1661), diffraction peaks which appear at $2\theta=20$, 24, 21.5 and 23 attribute to the $\alpha_1(100)$, $\alpha_2(002/202)$, $\gamma_1(001)$ and $\gamma_2(200)$ crystal planes of nylon 6, respectively. The diffraction peaks of the nylon crystals, indicated typical $\alpha_2(002/202)$ and $\gamma_1(001)$ form of nylon crystals.
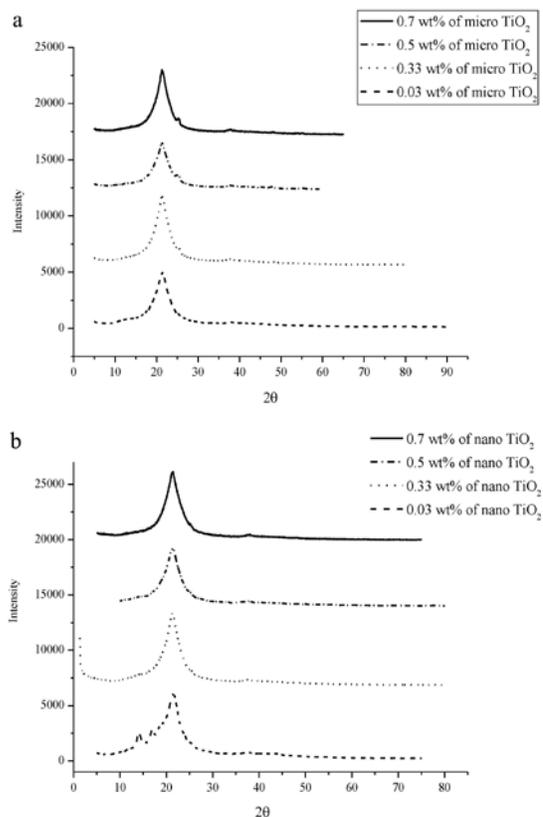

FIGURE 4. XRD graph of Nylon 6/TiO_2 micro (a) and nano (b) composite containing different amounts of TiO_2.

TABLE I. XRD results of Nylon 6/TiO$_2$ micro and nano-composite containing different amounts of TiO$_2$.

Sample Type	Weight percentages of TiO$_2$ (%)	TiO$_2$ (Anatase) (%)	TiO$_2$ (Rutile) (%)	Crystal size (nm)
TiO$_2$	-	80	20	19.45
Nano composite	0.03	81.1	18.9	9.39
	0.33	-	-	13.26
	0.5	86.7	13.3	19.24
	0.7	83.7	16.3	26.84
Micro composite	0.03	-	-	15.29
	0.33	86.9	13.1	23.92
	0.5	97.5	2.5	402.54
	0.7	86.9	13.1	402.445

As shown in *Figure 4*, the diffraction patterns of Nylon 6 crystals do not indicate any significant change; however, the degree of crystallinity (the intensity and height of peaks) for nano-particles is higher as compared to micro-particles. It might suggest that the smaller nano-sized TiO$_2$ had stronger effect on crystalline phase of nylon.

The X-ray crystallite size (D) was estimated from the anatase (101) diffraction peak using the Scherrer Eq. (1), and the results show a size of about 27 nm.

Mechanical Properties

It is believed that the mechanical properties of particle-filled polymer composites depend on several factors such as filler orientation, filler shape and size, dispersion of particles in the matrix, interaction of matrix with particles, and filler–filler interaction [14, 40, 42, 48, 54].

In order to test the effect of TiO$_2$ particles on physical property of nylon composite, the elongation at break and tenacity, which are both important characteristics for textile material, were measured. Elongation at break and tenacity values of Nylon 6 yarns containing different amounts of micro and nano titanium dioxide are given in *Table II*.

TABLE II. Physical properties of Nylon 6/TiO$_2$ micro and nano-composite containing different amounts of TiO$_2$.

Sample Type	Weight percentages of TiO$_2$ (%)	Tenacity (cN/Tex)	Elongation (%)
Neat	0	0.32	1662
Nano	0.03	1.19	386.8
	0.33	1.44	527
	0.5	0.49	210.6
	0.7	0.40	686
Micro	0.03	0.54	206.3
	0.33	0.87	409.8
	0.5	0.47	259.6
	0.7	0.36	287.1

Tenacity of nylon yarns incorporating different amounts of TiO$_2$ micro and nano-particles are higher than that of the pure one. Also it was found that the mechanical strength of the Nylon-6 with nano-particles was greater than with micro-particles. The mechanical strength of the Nylon 6 composite up to 0.33 wt % TiO$_2$ increased, and then decreased with increasing TiO$_2$ content.

This increasing in mechanical properties can be attributed to an additional energy-dissipating mechanism (mobility of the particles) introduced by the particles in Nylon 6 due to their good distribution throughout the composites. Because of aggregation, the size of the particles increased, therefore the mobility of particles was restricted. Consequently, the ability of the particles to dissipate energy was also reduced, which decreased the mechanical strength [55-57].

At high TiO$_2$ particle loading, filler–filler interaction results in agglomerated morphology. Agglomeration of particles yields a reduction of the aspect ratio of the TiO$_2$ particles and thus reduces the contact surface between particles and the polymer matrix. In addition, the agglomerated TiO$_2$ particles may also act as stress concentration sites in the composites. Thus, when subjected to tensile mode deformation, particles detach and debound from the polymer matrix. Bigger particles induce higher stress concentrations into the matrix and also lead to a reduction in impact energy. Consequently crack propagation could initiate locally, and, therefore, the final failure appears earlier [13, 14, 47-49, 54, 58-60].

As it is evident, compared with the unfilled filament, the addition of TiO$_2$ particles decreases the elongation at break whose values depends on the filler/matrix interaction. Excessively strong matrix–filler interaction causes a loss of flexibility of the polymer at the particle surface which depends mainly on the dispersion state of the fillers, resulting in a lowered elongation at break. The decrease in elongation at break in filled polymer composites is due to the fact that TiO$_2$ particles are rigid and have a higher modulus than the polymer and deformation of TiO$_2$ particles are generally much less than that of the polymer matrix and commonly increase the stiffness of the composite; thus, most of the deformations come from the polymer. The elongation at break of composites may also be reduced with rising filler content due to the inhomogeneous dispersion of particles.

It was found that the elongation at break of nano-composites was higher than the micro-composites which mean that the nano-composites do not become more brittle under high strain rate conditions. This suggests that the nano-particles are able to introduce

additional mechanisms of failure and energy consumption without heavily blocking the matrix deformation [14, 47, 48, 54, 61-64].

CONCLUSION
In this study, Nylon 6/TiO$_2$ composite multifilament yarns were prepared through melt spinning by mixing different amounts of TiO$_2$ particles (0.03, 0.33, 0.5 and 0.7) in two distinct sizes (nano and micro scale) with Nylon 6. SEM images of TiO$_2$-incorporated Nylon 6 composite clearly indicate that the TiO$_2$ nano-particles were uniformly incorporated into multifilament yarns with nearly spherical shape, whereas the micro-scaled titanium dioxide fillers formed non-spherical clusters, which were dispersed on the nylon matrix surface. In addition, the dispersion of TiO$_2$ in the composites was also investigated using TEM in which the result is in good agreement with SEM results. Energy dispersive x-ray analysis (EDX) confirmed the presence of titanium dioxide in the fibers. XRD patterns proved the existence of TiO$_2$ particles on the composite surface. The XRD analysis showed that TiO$_2$ particles consist of anatase and rutile structure which exist in all different multifilament composites. As shown by the XRD peaks, the typical γ_1 (001) form of the nylon crystals was the dominate observed peak for all filaments. The analysis of mechanical properties revealed that TiO$_2$ particles increased the tenacity but decreased the elongation at break of Nylon 6-based multifilament yarns. On the aspect of mechanical function, the nano TiO$_2$-incorporated Nylon 6 multifilament yarns proved to be more effective compared to micro ones, due to particle size. Tenacity first showed an increase followed by a decrease at higher loading. The reduction of tenacity at higher loading is the result of particle–particle interaction leading to agglomeration.

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