



## Production of Polyamide 6 Filled with Nano TiO<sub>2</sub>: Effect of Temperature, Strength and Dyeing

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The advent of nanotechnology has invigorated textile industry. This paper reports the results of an investigation aiming at finding what affect the nano TiO<sub>2</sub> powder during extruding polyamide 6. Polyamide 6 with 0.03 % TiO<sub>2</sub> was blended with various amounts of industrial and Degussa P-25 nano TiO<sub>2</sub> (0.03, 0.33, 0.5 and 0.7 %) and extruded in order to obtain polyamide 6 fibers containing industrial and nano TiO<sub>2</sub>. The crystalline size and phase of the powder have been characterized by X-ray diffraction. Energy dispersive X-ray microanalysis (EDX) showed the existence percent of nano TiO<sub>2</sub> on surface of yarns and the scanning electron microscopy showed the nano particles pervade on the samples. Strength test of samples had good results in compare with the samples that had industrial TiO<sub>2</sub> with the same per cent. The results show that from low TiO<sub>2</sub> concentrations, the strength of nano filled fibers increase till about 0.65 % TiO<sub>2</sub> and from this point, it suddenly drops down. The differential thermal analysis/thermal gravimetric analysis (DTA/TGA) test was done in order to calculate nano TiO<sub>2</sub> pervade and ashing test used too. All of these tests had almost the same results and proved used amounts of nano TiO<sub>2</sub> in samples. Differential scanning calorimeter was used for calculating crystalline per cent of fibers. Samples were dyed with acid carmosine red 14 (CI 14720, 1 g/L) and dye adsorbing was investigated by reflectance spectrophotometer and was compared with industrial samples.

**Key Words:** Nano TiO<sub>2</sub>, Polyamide 6, Dyeing, Strength.

### INTRODUCTION

Today, a wide range of nanoparticles and nano structures can be immobilized on fibers, which brings new properties to the final clothing product. In recent years, photo catalytic activity of TiO<sub>2</sub> has gained much attention because of its abilities to purify pollutions<sup>1,2</sup>. Dispersing of nano scale materials such as TiO<sub>2</sub> within polymeric matrices (nano composites) improve their properties such as strength, electrical conductivity, wettability and dyeability, depending on type and content of nano materials used<sup>3-8</sup>. These nano composites are usually produced with the diameter of 30 μm through melt spinning, wet (solution) spinning and sol-gel technology, but melt spinning is the most attractive method because of its low cost and high productivity<sup>9-10</sup>.

The main application of TiO<sub>2</sub> is in adsorbents and catalytic supports and in pigment. In almost all of these cases, the size of the titanium dioxide particles is an important factor affecting the performance of the materials<sup>11</sup>.

TiO<sub>2</sub> can exist in both crystalline and amorphous forms. In the case of photo catalytic, amorphous form is inactive. There are three crystalline phases of TiO<sub>2</sub>: anatase, rutile and brookite. Anatase and rutile are both tetragonal in structure while the brookite structure is orthorhombic<sup>12</sup>.

Polyamide 6 has a wide application in industry because of its good properties. In general, polyamide 6 fiber are produced as dull containing more than 0.5 % TiO<sub>2</sub>, semi dull containing between 0.3 % and 0.5 % TiO<sub>2</sub> and bright, containing about 0.03 % TiO<sub>2</sub><sup>13-15</sup>.

Most of the polyamide fibers dyed with acid, dispers, reactive and mordant dyes, but acid dye is most useful because of its excellent fastness properties, good solubility and variety of colours<sup>16,17</sup>.

The present study deals with effect of nano TiO<sub>2</sub> on physical properties of produced polyamide 6. The goals of this manuscript are to (i) produce polyamide 6 containing nano TiO<sub>2</sub>, (ii) characterize effect of temperature on strength of produced polyamide 6 fibers, (iii) evaluate dyeability of produced samples and compare them to industrial samples.

### EXPERIMENTAL

**Sample preparation:** The materials under investigation were polyamide 6 chips with 0.03 % dioxide titanium; nano TiO<sub>2</sub> supplied by Degussa P25. The polyamide 6 chips and nano TiO<sub>2</sub> were dried for 2 h at 900 °C to avoid samples oxidation. For blending, Twin Screw Extruder, DSE25, Brabender, Germany had been used. After extruding, the fibers enter the quenching air stream, which can come from the side of the

filaments and the accelerated filaments solidify in the cool air at a temperature of 20 °C. To achieve a good dispersion of the TiO<sub>2</sub> particles, the obtained polyamide 6/TiO<sub>2</sub> granule extruded under the same condition for second time and the fibers with linear density of 0.56 tex was obtained<sup>13,18</sup>. The Specification of fiber samples are presented in Table-1.

Sample code	Type of TiO <sub>2</sub>	Used TiO <sub>2</sub> (%)
A	Nano	0.03
B	Nano	0.33
C	Nano	0.50
D	Nano	0.70
E	Industrial (un-nano)	0.03
F	Industrial (un-nano)	0.33
G	Industrial (un-nano)	0.50
H	Industrial (un-nano)	0.70

**Characterization:** X-ray diffraction analysis was carried out for crystal phase identification of the TiO<sub>2</sub> samples using a Bruker, D8ADVANCE, Germany; X-ray tube anode: Cu; wavelength: 1.5406 Å (CuK<sub>α</sub>); Filter: Ni.

Thermal gravimetric analysis/differential thermal analysis was performed in Shimadzu DTG-50H at the heating rate of 10 °C/min. Scanning electron microscopy photos of specimens were obtained by Philips, XL30, Netherlands and the specimens were coated by gold with P.V.D method. Energy dispersive X-ray of specimens was prepared coincide of SEM. The crystalline per cent of specimens was investigated by differential scanning calorimeter (DSC), Shimadzu-50, ASTM D3895-95. Reflectance spectrophotometer (BYK-Garden-CIELAB 1976-India) with D65 light source was used for investigation of samples dye adsorption.

Strength test was performed by ISO 5079-breaking strength of fibers. The test was performed at room temperature (T = 22 °C) and at freezing temperature (T = - 5 °C). For dyeing, acid carmosin red 14 (CI 14720, 1 g/L) was used.

**Dyeing:** The dyeing behaviour of the acidic dye (caromosin red 14, CI 1470) (Fig. 1) on nylon 6 was investigated. Produced polyamide 6 fiber was immersed in the dyebath. Dyeing was started at 20 °C and the temperature rose by 2 °C min<sup>-1</sup> to 80 °C. Dyeing was continued for 45 min at this temperature and then the fibers were washed with distilled water<sup>19</sup>.

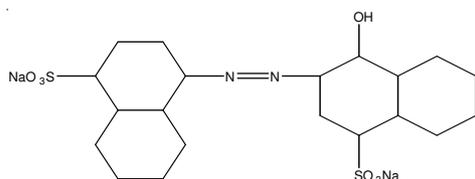


Fig. 1. Structure of acid carmosin red 14

## RESULTS AND DISCUSSION

**Particle size and crystal phase:** Diameter of nano TiO<sub>2</sub> particle size is 21 nm reported by Degussa company. The XRD spectra of the nano TiO<sub>2</sub> is shown in Fig. 2. Two peaks of anatase and rutile observed for P 25. Quantification analysis showed that the average percentage of anatase and rutile was

84 % and 16 % respectively and the crystal size was 16.6 nm, while the crystal size of industrial TiO<sub>2</sub> was 0.3 μm but with the same phases percentage.

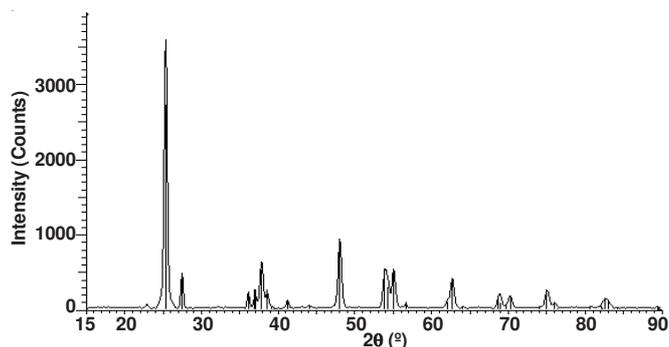


Fig. 2. Spectra of nano TiO<sub>2</sub> and crystal phase percent

### Scanning electron microscopy, energy dispersive X-ray and distribution of nano particles:

Scanning electron microscopy photo of nano TiO<sub>2</sub> is illustrated in Fig. 3. The intensity of electrons was 15 kv. The SEM of polyamide 6 fibers prove the distribution of nano particles on filaments and as shown in photos, the difference between industrial and nano filed fibers are clear in sample H and D (Figs. 4-6). Energy dispersive X-ray (EDX) microanalysis was employed to establish the chemical identity of the observed particles. It can be clearly seen from the EDX analysis (Fig. 7) that particles existing on the surface of fibers are titanium dioxide particles pervading onto fibers surface. Energy dispersive X-ray of specimens show the per cent of material just on the surface of fibers. However, in these filaments, nano particles pervade on and in the fibers, so for proving distribution of nano particles in fibers ashing test, DTA/TGA was used and concentration of TiO<sub>2</sub> particles in filaments was obtained (Table-2).

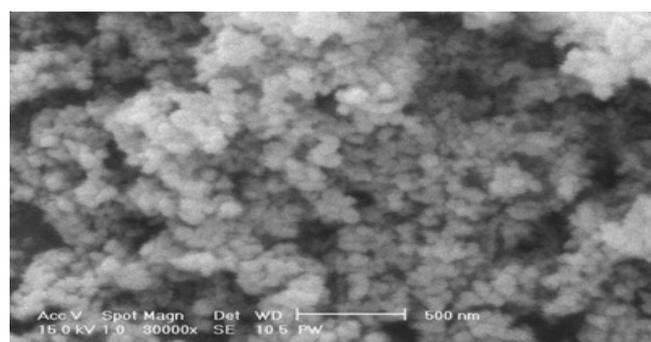


Fig. 3. Scanning electron microscopy of nano TiO<sub>2</sub> powder

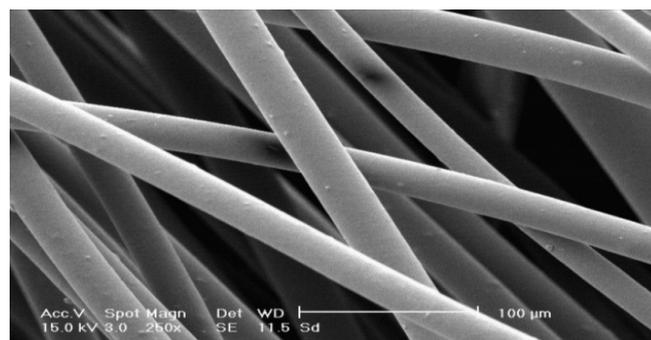


Fig. 4. Scanning electron microscopy of sample D fiber containing nano TiO<sub>2</sub>

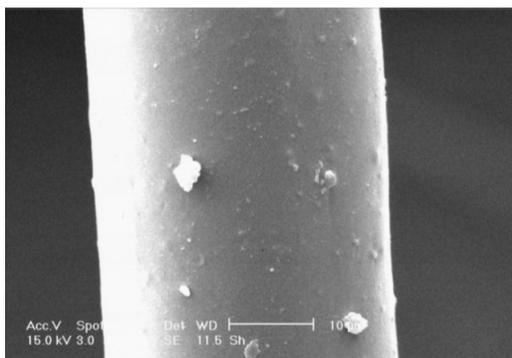


Fig. 5. Scanning electron microscopy of sample H fiber containing TiO<sub>2</sub>

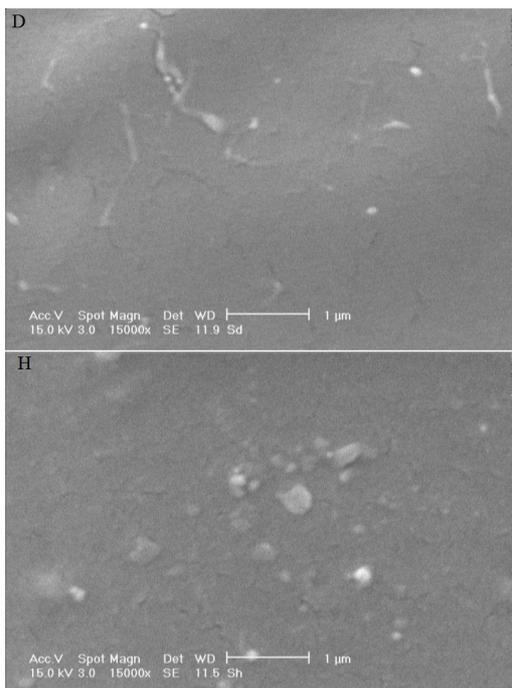


Fig. 6. Scanning electron microscopy comparisons of sample H and D

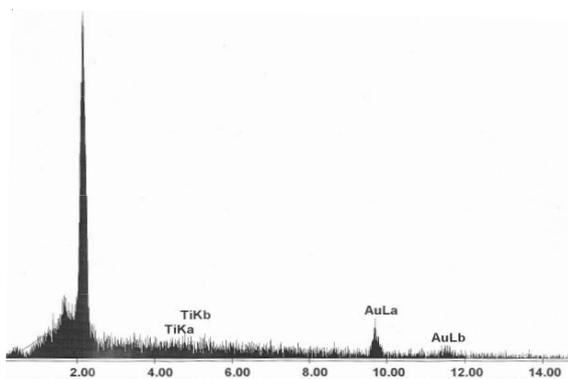


Fig. 7. EDAX of sample D fiber containing nano TiO<sub>2</sub>

TABLE-2 RESULTS OF TiO <sub>2</sub> % BY TWO METHODS				
Sample	Used % of nano TiO <sub>2</sub>	TiO <sub>2</sub> % by ashing method	TiO <sub>2</sub> % by DTA/TGA method	EDX
A	0.03	0.041	0.033	0.01
B	0.33	0.357	0.301	0.19
C	0.50	0.496	0.429	0.32
D	0.70	0.705	0.682	0.41

**Nano particle concentration in fiber:** Two methods were used for evaluation of nano particles per cent in polyamide filaments; DTA/TGA test and ashing test. In DTA/TGA, thermal analysis was done for blank and produced filaments and by calculating the remain particles, the per cent of nano TiO<sub>2</sub> was obtained<sup>20</sup>.

In the ashing test, 5 measured samples contain a blank one, was burned in stove at 660 °C for 2 h and the remaining ash were measured and the per cent of nano particles was calculated. Table-2 show the results of ashing test in a good agreement with the results of DTA/TGA<sup>21</sup>.

**Differential scanning calorimetry:** Differential scanning calorimetry (DSC) gives information on the transitions that take place in the material due to heating. The changes in these transitions assist to identify the structural changes that have happened in samples<sup>22</sup>. The fibers of polyamide 6 and nano filled polyamide 6 were characterized by DSC and melting and their crystallization behaviour was studied. Fibers were heated to 260 °C under nitrogen flow and were maintained at this temperature in order to destroy thermal history related to the processing and to the shear stresses generated during extrusion. At this time, the melting points of samples were evaluated. The samples were then cooled to 20 °C and melting point and enthalpy were calculated<sup>23,24</sup>.

The crystalline per cent of samples was calculated through formula 1<sup>25</sup>. Table-3 shows the crystalline per cent of fibers. It is evident from Table-3 that the crystallinity of polyamide 6 shifts to a higher per cent with the increase of TiO<sub>2</sub> percent<sup>12,15</sup>. Fig. 8 show the DSC graph of sample D.

$$\% C = \frac{\Delta H_m}{\Delta H_0} \tag{1}$$

where, % C: crystal per cent of specimen; ΔH<sub>m</sub>: specimen melting enthalpy (J/g); ΔH<sub>0</sub>: melting enthalpy of 100 % crystalline polyamide 6 (J/g).

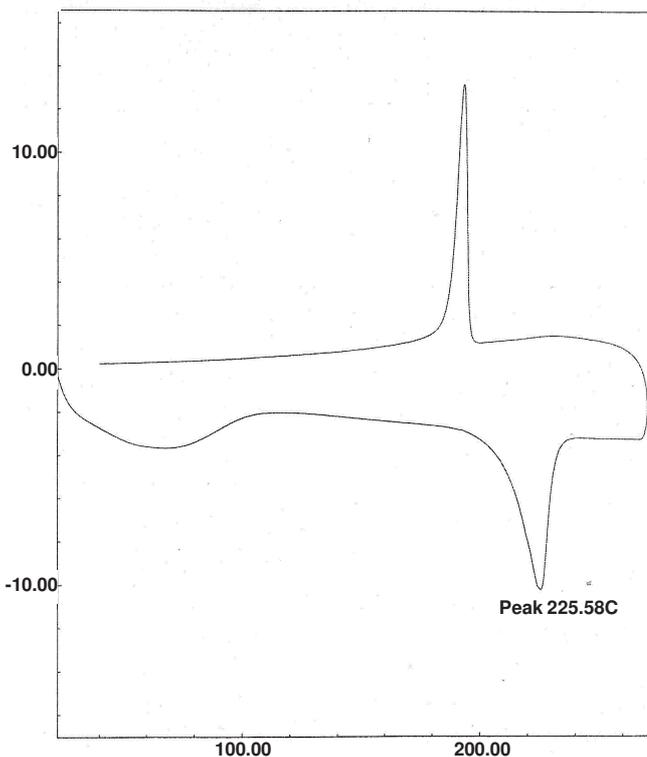


TABLE-3  
STRENGTH AND CRYSTAL PERCENT OF SAMPLES

Sample	T = 23 C			T = -5 C			Crystalline (%)
	Strength (N/tex)	Elongation (%)	Breaking force (N)	Strength (N/tex)	Elongation (%)	Breaking force (N)	
A	0.684	319.7	0.3830	0.500	316.0	0.2800	58
B	0.646	294.0	0.3620	0.457	286.9	0.2559	62
C	0.622	269.7	0.3488	0.378	259.0	0.2116	65
D	0.254	166.0	0.1424	0.225	160.2	0.1260	66
E	0.642	272.1	0.3600	0.486	263.6	0.2721	51
F	0.581	246.8	0.3253	0.427	238.7	0.2391	59
G	0.547	218.5	0.3068	0.347	205.3	0.1943	64
H	0.398	172.4	0.2228	0.315	168.8	0.1764	68

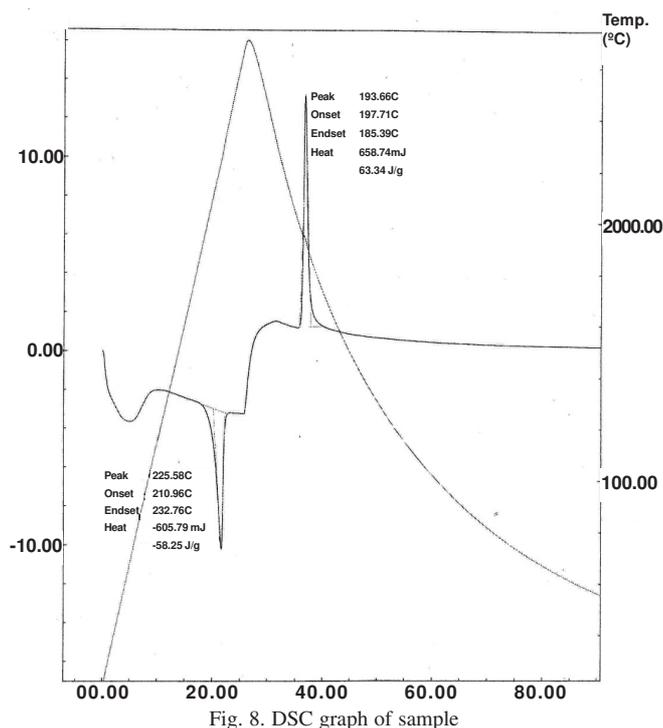


Fig. 8. DSC graph of sample

**Effect of temperature:** The strength of fibers was investigated by ISO 5079-Breaking strength of fibers test method. The linear density of fibers was 0.56 tex. For each sample, 30 fibers were tested using ANOVA table and the data were standard by Duncan method. The results are presented in Table-3. As shown, the strength of fibers changes significantly with increase in temperature. It means that by increasing temperature (from freezing to room), the strength of fibers increased with no exception<sup>2</sup>. In higher temperature the humidity reduce and in lower temperature this humidity plays the role of plasticizer and cause the motion of macromolecular chains of the polymer<sup>26</sup>.

The effect of TiO<sub>2</sub> per cent is quiet pronounced: the lower the TiO<sub>2</sub> per cent is, the lower the crystallinity and the higher the strength is. The characteristic of strength is similar for both materials. The stress-strain curve of fibers is presented in Fig. 9.

By comparing the strength of TiO<sub>2</sub> and nano TiO<sub>2</sub> filled fiber, it is delineated that the strength of nano filled fibers are higher than industrial ones till 0.65 % TiO<sub>2</sub> (turning point) and from this point, it suddenly drops down. So, lower particles size lead to improved mechanical properties of the fibers such as strength, in general<sup>26,27</sup>.

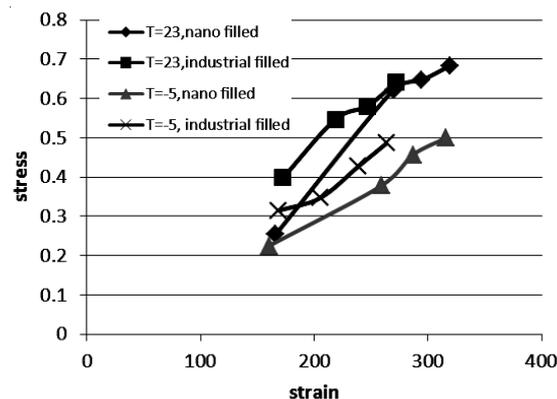
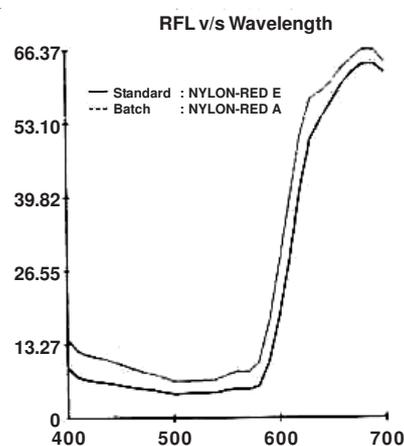


Fig. 9. Stress-strain graph of fibers

**Effect of dyeing:** The changes in dye absorbance of fibers were monitored using a reflectance spectrophotometer. The instrument analyzes the light being reflected from the sample and produces an absorption spectrum<sup>1</sup>. Due to the colouring of fibers provided by the TiO<sub>2</sub> nanoparticles and industrial particles, it can be observed that dye adsorption of nano filled fiber is higher than the other one except in lower concentration (sample A) (Figs. 10-13). So, nano TiO<sub>2</sub> use and its effect on filaments occur in a special range of nano TiO<sub>2</sub>, considering that before and after this range, it doesn't have the same effect, as it was reported in previous works<sup>28</sup>. So, the dye adsorption was found to be sensitive not only to the mass concentration of TiO<sub>2</sub> but also effect by type of TiO<sub>2</sub>. The comparison of dye adsorption and effect of TiO<sub>2</sub> % in polyamide 6 fibers are presented in Fig. 14.

Fig. 10. Reflection of nano samples and usual samples with same TiO<sub>2</sub> per cent (0.03%)

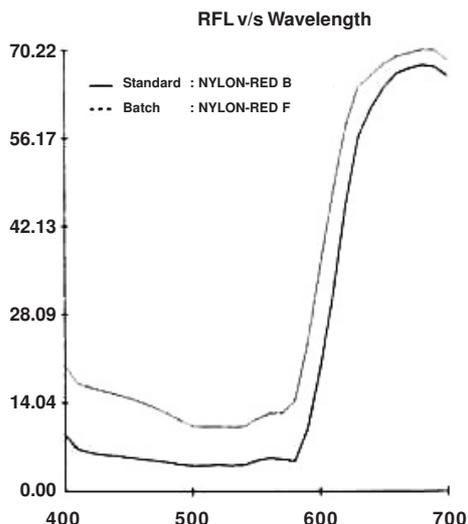


Fig. 11. Reflection of nano samples and usual samples with same TiO<sub>2</sub> per cent (0.33 %)

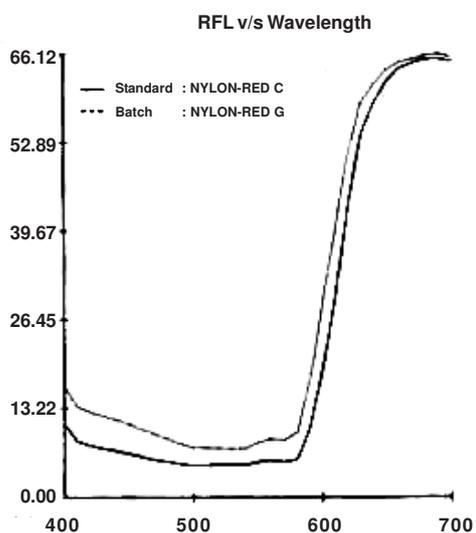


Fig. 12. Reflection of nano samples and usual samples with same TiO<sub>2</sub> per cent (0.5 %)

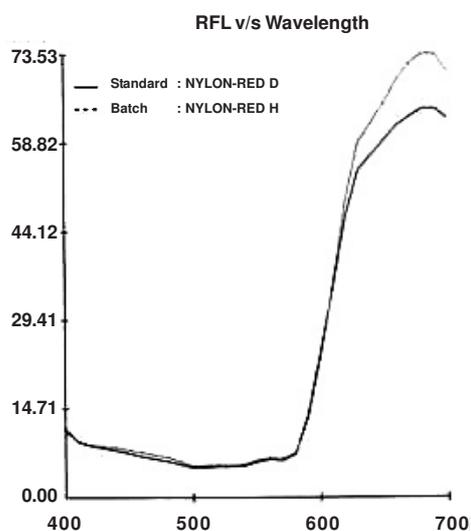


Fig. 13. Reflection of nano samples and usual samples with same TiO<sub>2</sub> per cent (0.7 %)

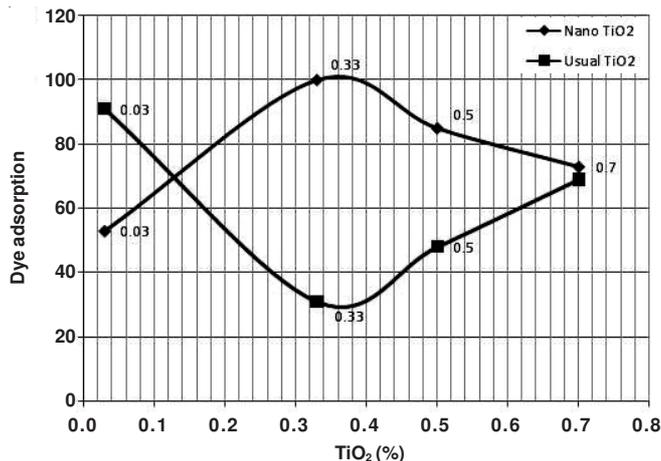


Fig. 14. Curve of dye adsorption of sample

**Conclusion**

This study was undertaken to investigate the behaviour of polyamide 6 fiber generated by twin screw extruder containing nano and industrial TiO<sub>2</sub> under different test conditions. With the exception of the highest TiO<sub>2</sub> concentration, the strength and crystallinity of nano filled fibers was shown to be higher than industrial ones, both in room and freezing conditions. The results indicate that TiO<sub>2</sub> per cent has a direct relationship with crystallinity and an inverse relationship with strength. From specific quantity of nano TiO<sub>2</sub>, the dye adsorption of nano filled fibers are increase compared with the other and the peak of adsorption reaches to 0.33 % nano TiO<sub>2</sub>, whereas the adsorption of industrial fibers reduces and from this point (33 %) it increase and reaches the nano filled adsorption. Hence, the dyeability of nano filled samples appears to be better than the others. In general, using nano TiO<sub>2</sub> in spinning of polyamide 6 (in specific range) improves the properties of this fiber, causes to improve the strength, increases the crystalline per cent and almost improves the dyeability of this kind of fiber.

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