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# Effect of Delustering Agent on Physical and Mechanical Properties of Nylon 6

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Titanium dioxide is one of the most important delustering agent additives in synthetic fiber production, as nylon. Different amounts of $TiO_2$ are used to gain various characteristics on synthetic fibers in industrial applications. In this research two types of nylon granules were processed with different amounts of $TiO_2$ (0.30 and 0.03 %). Then, two types of yarn were created using circular shape spinneret from the mentioned granules. The effects of $TiO_2$ on physical, mechanical, thermal and morphological properties of granules and prepared yarns were studied. Results showed that by increasing the amount of $TiO_2$, strength of yarns decreased. Thermogravimetric analysis showed that with enhancement in the amount of $TiO_2$, degradation temperature was decreased. The reduction in the crystalline part was the reason for this temperature variation, as it was also proved by DSC analysis. Morphology of yarns was further studied using scanning electron microscopy (SEM), which shows an increase in the amount of $TiO_2$ on the fiber surface, by increasing the overall amount of $TiO_2$. Results indicate the improvement in dye adsorption by increasing the amount of $TiO_2$.

**Key Words: Delustering agent, Mechanical properties, Nylon 6, Physical properties.**

## INTRODUCTION

One of the most famous delustering agents is titanium dioxide. There is a growing interest in development of composites consisting of organic polymers and titania ($TiO_2$). This is based on positively perceived characteristics of these composites; such characteristics include mechanical performance, thermal properties, biodegradability and optical properties[1-7]. In textile industry, titanium dioxide ($TiO_2$) is used as an additive for matting and gloss reduction of synthetic fibers[8,9]. The added amount depends on the desired degree of matting (Table-1)[10]. Titanium dioxide exists in both crystalline and amorphous forms. In the case of delustering, crystalline form is inactive. There are three crystalline phases of $TiO_2$: anatase, rutile and brookite. anatase and rutile are both tetragonal in structure while the brookite structure is orthorhombic[11].

TABLE-1
DIFFERENT AMOUNT OF $TiO_2$ FOR MATTING

| $TiO_2$-content (%) | Type of yarn |
|---|---|
| < 0.03 | Super bright |
| 0.03-0.05 | Bright |
| 0.15-0.35 | Semi dull |
| 0.45-1.00 | Dull |
| > 1-4 % | Full dull |

Usable forms of $TiO_2$ in fiber production are divided in two types of anatase and rutile. Rutile pigments are only used in polypropylene fibers, but anatase pigments are used in nylon and other synthetic fibers. This paper presents the influence of titania quantity on nylon-6 granules and yarns properties, such as thermal, mechanical, optical and dyeability.

## EXPERIMENTAL

The materials used in this study are caprolactam, dispersing agent (amino propyl morpholin), titanium dioxide, acid dye (acid blue 62), acetic acid. Caprolactam was supplied by BASF. Titanium dioxide was supplied by Sachtleben (Table-2). Dispersing agent (amino propyl morpholin) and acetic acid were supplied by Merck and Telon blue RR (acid blue 62) as acid dye was supplied by Dystar (Fig. 1).

### Methods

**Caprolactom polymerization:** Polymerization process carried out according to commercial process used for nylon-6 fiber production at Alyaf Tehran Company. A suspension of titania (0.3 and 0.03 % w/w), water (75 L), melted caprolactam (75 L) and 4-3 aminopropylmorpholine (as dispersing agent; 2 L) added to the polymerization reactor. Hereby nylon-6 granules produced (Table-3).

TABLE-2
DATA OF $TiO_2$ ANATASE FORM WITHOUT $SiO_2$ SURFACE COATING

| Material | Min | Max | Typical |
|---|---|---|---|
| $TiO_2$ (Anatase) (%) | 94.8 | 96.60 | 95.70 |
| $TiO_2$ (Rutile) (%) | – | 2.00 | 0.70 |
| Sb (%) | 0.26 | 0.34 | 0.30 |
| P (%) | 0.35 | 0.61 | 0.48 |
| Al (%) | 0.58 | 0.90 | 0.74 |
| Si (%) | – | 0.18 | 0.14 |
| Mn (%) | 0.15 | 0.28 | 0.21 |
| Fe (mg/kg) | – | 50.00 | 35.00 |

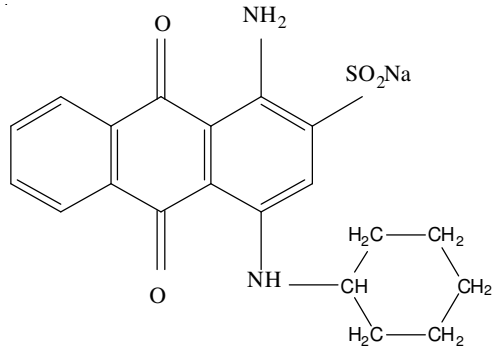



Fig. 1. C.I. acid blue 62

TABLE-3
PROPERTIES OF PRODUCED NYLON-6 GRANULES

| $TiO_2$ (%) in polymer | MFI in 235 ºC and 5 g load (g/10 min) | Granule shape | Relative viscosity (η) |
|---|---|---|---|
| 0.03 | 48.2 | Cylindrical | 2.47 |
| 0.30 | 55.2 | Cylindrical | 2.32 |

**Sample preparation:** At first step, granules were dehydrated for 2 h at 80 ºC. The used injection equipment was Aslanian-EM80 and the injection temperature gradient from the funnel toward the injection nozzle was 220, 230 and 235 ºC, respectively. Dumbbell shaped samples used for the tension test and creviced samples used for the impact test were produced using injection molding in standard molds with the dimensions according to ASTM D638 standard. Samples were prepared with the thickness of 4 mm and the width of measurement area of 10 mm.

**Fiber spinning:** All the processing parameters were the same as commercial process according to Table-4. Two kinds of multifilament yarns (named semidull and bright) produced of prepared granules by circular shape of spinneret (Table-5).

TABLE-5
SPECIFICATION OF PRODUCED YARNS

| Sample code | Yarn type | Fiber cross section | $TiO_2$ (%) | Yarn density (denier) | Spinneret hole number |
|---|---|---|---|---|---|
| B | Semidull | O | 0.3 | 40 | 10 |
| A | Bright | O | 0.03 | 40 | 10 |

## Detection method

**Rheological properties:** Rheological measurements were performed using a rotational rheometer (Rheometrics, Inc.) with parallel plate geometry (plate diameter = 25 mm). The compression-molded plaques were used for measurements at 245 ºC after drying at 80 ºC in a vacuum oven for 24 h, in order to prevent moisture-induced degradation phenomena. All measurements were performed with a force transducer with a range of 0.2-200 g cm torques. Typical samples thickness ranged from 1.2-1.5 mm. The rheological measurements were carried out, as follow: dynamic frequency sweep test over a frequency range of 0.01-1000 rad/s.

## Thermal analysis

**Differential scanning calorimetry:** NETZSCH_200F3 Maia (Germany) differential scanning calorimetry (DSC) was used to determine the influence of Titana content on the crystallization behaviour of the nylon-6 yarns. The test samples (about 5 mg) were first heated from 20-280 ºC at a heating rate of 10 ºC/min and then held at 280 ºC for 2 min before cooling down in order to assure that the materials melted uniformly and to eliminate the thermal history. The samples were then cooled to 20 ºC and held 2 min before reheating to 280 ºC. The cooling rate was 10 ºC/min. All measurements were conducted under a nitrogen atmosphere. The degree of crystallinity of the samples was calculated using the eqn. 1.

$$X(\%) = \left(\frac{\Delta H_F}{\Delta H_F^\circ}\right) \times 100 \quad (1)$$

where $\Delta H_F$ = heat of fusion determined by DSC and $\Delta H^\circ_F$ = heat of fusion of completely crystalline nylon-6[12]. Several different $\Delta H^\circ_F$ values for the perfect nylon-6 crystal have been reported, such as 190[13-16], 230[12] and 240 j/g[17,18]. The $\Delta H^\circ_F$ value of 240 j/g was used here to calculate the degree of crystallinity of nylon-6.

**Thermogravimetric analysis:** The thermogravimetric analysis (TGA) was performed on a PL_1500 thermoanalyzer according to ASTM E 1131_03. In each case, a 2 mg sample

TABLE-4
PARAMETERS FOR SPINNING OF FILAMENTS

| Extruder press | | | | | | | Through put | | Spinneret | | Quenching | | Take up | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Extruder zone set (ºC) | | | | | Flange temp (ºC) | Product temp. (ºC) | Extruder (g/min) | Spinneret (g/min) | No holes | Diameter (mm) | Air temp. (ºC)/hum % | Air flow rate (m/s) | Speed (m/min) | Draw |
| Zone # 1 | Zone # 2 | Zone # 3 | Zone # 4 | Zone # 5 | 272 | 270 | 654 | 10.22 | 10 | 35 | 17/80 | 0.35 | 800 | 3.4 |
| 28 2 | 28 0 | 27 8 | 27 6 | 27 4 | | | | | | | | | | |

was examined under a nitrogen flow rate of 50 mL/min at a heating rate of 10 ºC/min from room temperature to 650 ºC.

### Morphological characterization

**Scanning electron microscope (SEM):** The morphological properties of the samples were observed by scanning electron microscope (LEO 440i, Leo Electron Microscopy, Cambridge, England). The samples were coated with gold and observed under 20 keV accelerating voltage.

**Energy dispersive X-ray spectrometer (EDX):** The energy dispersive X-ray analysis of samples (yarns) were examined, using a scanning electron microscope (LEO 440i, Leo Electron Microscopy, Cambridge, England) equipped with an energy dispersive X-ray system (INCAX- Sight-England) for investigate the relative concentration of $TiO_2$ on surface of samples (yarns).

**Determination of dye bath exhaustion:** Telon blue RR (acid blue 62) was used for dyeing process of the yarns, dyeing ratio was 1:100, dye weight was 1 %/weight of the yarn and pH of the dye bath was 4.5 that was provided by adding acetic acid. A certain weight of the yarns was immersed into the dyeing solution for 10 min at 40 ºC, the solution was then heated up at a rate of 2 ºC/min to 80 ºC and kept constant for 50 min. Then, the effect of the amount of $TiO_2$ on the percentage of dye bath exhaustion was calculated according to eqn. 2:

$$\text{Exhaustion}(\%) = \left[\left(\frac{A_0 - A_d}{A_0}\right)\right] \times 100 \qquad (2)$$

where $A_0$ and $A_d$ are the absorbances (at $\lambda_{max}$) of the initial and the residual dye in the dyebath, respectively. The absorbances were measured by using a JENWAY 6505 UV-vis spectrophotometer.

### Mechanical properties

**Mechanical properties of granules:** The pre-conditioning was carried out in an air-conditioned room for at least 48 h at 23-25 ºC and 50-55 % relative humidity prior to measurements. The tensile tests were carried out according to ASTM D638. The tests were performed using INSTRON 6025 equipment and a crosshead speed of 10 mm $min^{-1}$. All data presented from mechanical tests represent an average of ten repeated measurements. Notched Izod impact measurements were made at room temperature according to ASTM D256 using ZWICK 5102 machine. The samples were stored in a desiccator under vacuum before tests.

**Mechanical properties of yarns:** Mechanical properties of produced nylon-6 yarns were measured using ZWICK 1446 tensile properties tester machine according to ASTM standard D2256-02. In order to obtain the tensile properties, the constant rate of elongation method was applied. The clamp speed was 800 mm/min and the initial length was 500 mm for all samples. Each sample was tested for 10 times to measure the accurate tensile properties and mechanical properties such as elongation at break and tenacity were reported.

## RESULTS AND DISCUSSION

**Rheological properties:** Fig. 2 shows that nylon-6 with 0.3 wt % $TiO_2$ exhibit higher complex viscosity than nylon-6 with 0.03 wt % $TiO_2$ at low frequencies, at temperature 245 ºC, respectively. Nylon-6 with 0.03 wt % $TiO_2$ exhibits Newtonian behaviour, while the nylon-6 with 0.3 wt % $TiO_2$ exhibit decreasing complex viscosity with increasing frequency.

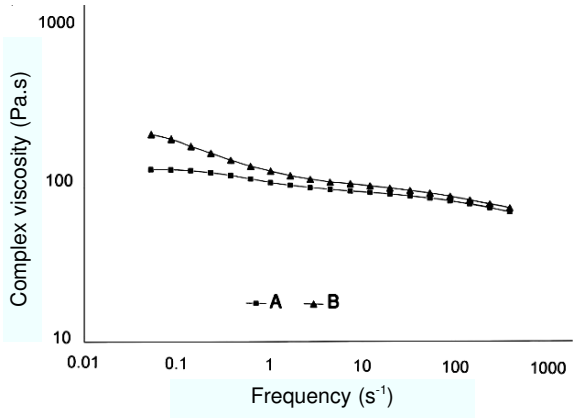



Fig. 2. Complex viscosity of samples at 245 ºC

Fig. 3 shows a viscoelastic dynamic oscillatory response and viscoelastic response as measured by the storage modulus (G') and the loss modulus (G") at temperature 245 ºC, respectively.

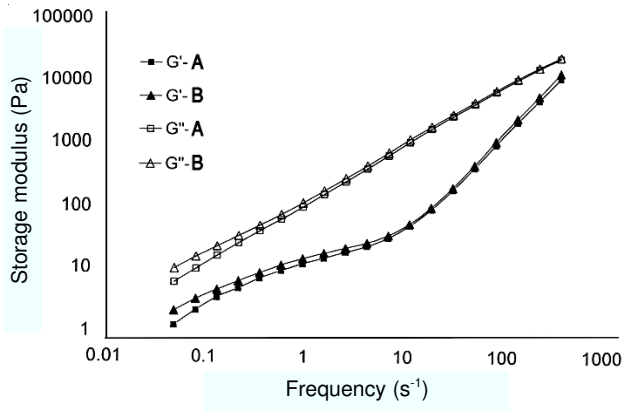



Fig. 3. Storage and loss modulus of samples at 245 ºC

Solid-like behaviour can be seen from the dynamic oscillatory response. Nylon-6 with 0.3 wt % $TiO_2$ demonstrate higher storage moduli at both low and high frequencies and exhibit more solid-like behaviour than nylon-6 with 0.03 wt % $TiO_2$.

### Thermal properties

**Thermogravimetric analysis (TGA):** The thermal degradation behaviour of samples (yarns), such as, initial, half and maximum degradation temperatures ($T_d$,$T_{da}$ and $T_{dm}$) of samples, are listed in Table-6. The titania loading effect on the degradation behaviour of the samples is observed in this data, obviously. The yarn with 0.3 wt % $TiO_2$ shows the lowest thermal stability among the samples. According to Table-6, the $T_d$,$T_{da}$ and $T_{dm}$ of samples decreased slightly with raising titania concentration.

**Differential scanning calorimetry (DSC):** Table-7 shows the crystallization behaviour of samples (yarns) obtained from DSC test. With increase in amount of $TiO_2$ in the samples $T_c$

TABLE-6
TGA VALUES OF PRODUCED NYLON-6 YARNS WITH DIFFERENT CROSS SECTION AND DIFFERENT AMOUNT OF $TiO_2$

| Sample code | Initial degradation temp. $T_d$ (ºC) | Temperature at half degradation $T_{da}$ | Temperature at max degradation $T_{dm}$ (ºC) |
|---|---|---|---|
| A | 301 | 461 | 569 |
| B | 271 | 445 | 493 |

TABLE-7
DIFFERENTIAL SCANNING CALORIMETRY DATA OF SAMPLES

| Sample code | Crystallization temp. ($T_c$) (ºC) | Melting temp. ($T_m$) (ºC) | Degree of crystallinity ($X_c$) % | Transition glass temp. ($T_g$) (ºC) | $\Delta H_m$ (J/g) |
|---|---|---|---|---|---|
| A | 188.22 | 234.72 | 30.64 | 86.7 | 73.54 |
| B | 186.23 | 228.71 | 26.34 | 77 | 63.21 |

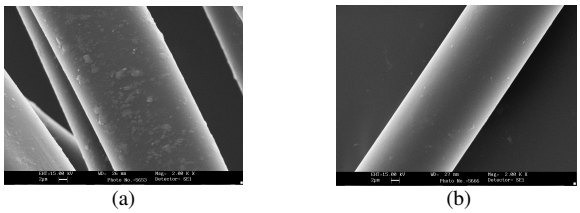
was approximately constant (with a very small difference). The degree of crystallinity ($X_c$) varied with change the amount of $TiO_2$ as shown in Table-7. Nylon-6 yarn with 0.03 wt % $TiO_2$ had higher $X_c$ than other sample. This is because these particles act as filler agents and there is no tendency in them to polymer chains, therefore it leads to a decrease in polymer chain orientation and degree of crystallinity as well. The magnitude of $X_c$ of these samples is: A > B.

Table-7 shows the melting values ($T_m$) of the samples, respectively. Nylon-6 yarn with 0.3 wt % $TiO_2$ had lower $T_m$. This can be a result of low content of crystallinity. The order of magnitude of $T_m$ for these samples is A > B.

Table-7 show the transition glass temperature ($T_g$) of different samples. Nylon-6 yarn with 0.3 wt % $TiO_2$ had lower $T_g$ than other, since despite of higher amounts of $TiO_2$, this particles are placed among the molecular chains and makes them more easier to move. The order of magnitude of $T_g$ for these samples is A > B.

## Morphological characterization

**Scanning electron microscopy (SEM):** The phase morphology of samples is represented in Fig. 4 (a-b). Fig. 4a shows the SEM micrograph of nylon-6 yarn with 0.3 wt % $TiO_2$. This shows that aggregates of $TiO_2$ particles were large as compared to nylon-6 yarns with 0.03 wt %. With decrease of $TiO_2$ particles in yarn, the aggregates were small and it is shown in Fig. 4b.



(a) (b)

Fig. 4. Scanning electron microscope micrograph of yarns with different amount of $TiO_2$. (a) Nylon-6 yarn with 0.3 % wt $TiO_2$ (b) Nylon-6 yarn 0.03 % wt $TiO_2$

**Energy dispersive X-ray spectrometer (EDX):** Figs. 5 and 6 show the EDX analysis of samples (yarns), it is clear

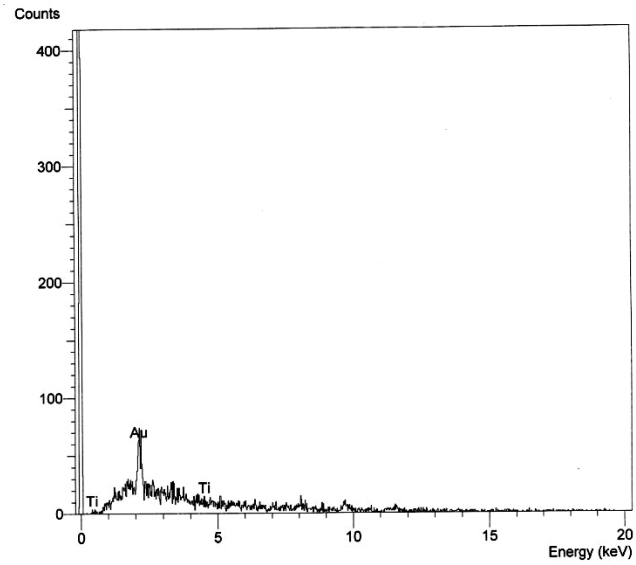



Fig. 5. EDX spectrum for nylon-6 yarn with 0.03 wt % $TiO_2$

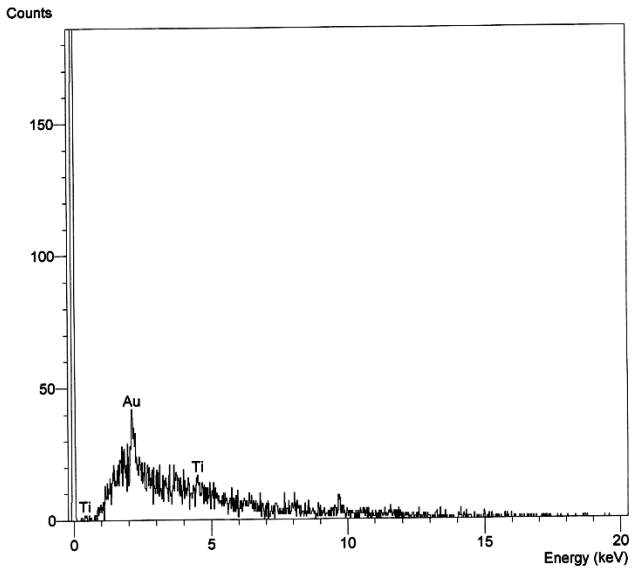



Fig. 6. EDX spectrum for nylon-6 yarn with 0.3 wt % $TiO_2$

that in all samples, titanium dioxide is detected. Fig. 6 shows with addition the amount of $TiO_2$ in fiber, the amount of $TiO_2$ on surface of fibers is increased.

**Determination of dye bath exhaustion:** Table-8 shows the exhaustion values for the samples (yarns) dyed with acid dye (acid blue 62). The dye showed higher exhaustion on the nylon yarn with 0.3 wt % $TiO_2$ comparing to other sample. This confirms that with increasing the amount of $TiO_2$, these particles are placed among the molecular chains and in this case, the distance among polymer chains in amorphous phase become greater so the diffusion of dye molecules increases in the fabric. On the other side, larger distance among polymer chains in amorphous phase provides more ending amino groups for acid dye adsorption. Regularly, dye adsorption takes place in three levels. First, dye absorption on fabric's surface; second, diffusion of dye in the fabric and third creation of bonds between dye and active groups in the fabric. As a result of former explanations, addition in the amount of $TiO_2$ eases levels 2 and 3 of dye adsorption[19,20].

TABLE-8
EXHAUSTION VALUES OF ACID DYE BY SAMPLES

| Sample code | $TiO_2$ (%) | Fiber cross section | Exhaustion (%) |
|---|---|---|---|
| A | 0.03 | Circular | 57 |
| B | 0.30 | Circular | 75 |

**Mechanical properties of granules and yarns:** With respect to Tables 9 and 10, it is observed that by increasing the amount of $TiO_2$, tenacity of samples (granules and yarns) decreases. Generally, tenacity of yarns is evaluated by orientation of polymer chains. Therefore, the results from tenacity tests correspond with the results from thermal analysis of the samples, because by increasing the amount of $TiO_2$, the crystallinity decreased (by studying the extracted data from DSC). This is because these particles act as filler agents and there is no tendency in them to polymer chains, therefore the polymer chains obtain more freedom in their movement and respectively, there is a decrease in their strength and also an increase in their elongation. Elongation at break also increased similar to the tenacity of yarns by increasing the amount of $TiO_2$, according to Table-8.

TABLE-9
MECHANICAL PROPERTIES OF PRODUCED NYLON-6 YARNS WITH DIFFERENT AMOUNT OF $TiO_2$

| Sample code | Yarn type | Fiber cross section | $TiO_2$ (%) | Tenacity (g/den) | Elongation (%) |
|---|---|---|---|---|---|
| A | Bright | O | 0.03 | 5.31 | 41.36 |
| B | Semidull | O | 0.3 | 4.7 | 46.27 |

TABLE-10
MECHANICAL PROPERTIES OF PRODUCED NYLON-6 GRANULES WITH DIFFERENT AMOUNT OF $TiO_2$

| Sample | Stress at yield point (MPa) | Strain at yield point (%) | Stress at brake (MPa) | Strain at brake (%) | Tensile modulus (MPa) | Impact resistance | |
|---|---|---|---|---|---|---|---|
| | Mean | Mean | Mean | Mean | Mean | Mean | SD |
| A | 65.3 | 1.9 | 57.3 | 3.9 | 5967 | 33.9 | 17.12 |
| B | 64.8 | 2.9 | 44.9 | 42.8 | 5389 | 27.3 | 7.98 |

## Conclusion

The effect of delustering agent (titania) content on the mechanical, thermal, rheological and morphological properties of granules and prepared nylon-6 yarns was investigated.

Results showed that by increasing the amount of $TiO_2$, strength of granules and yarns decreased. This is because these particles act as filler agents and there is no tendency in them to polymer chains, therefore the polymer chains obtain more freedom in their movement and, respectively, there is a decrease in their strength and also an increase in their elongation. Thermogravimetric analysis showed that with enhancement in the amount of $TiO_2$, degradation temperature was decreased. The reduction in the crystalline part was the reason for this temperature variation, as it was also proved by DSC analysis. Morphology of yarns was further studied using scanning electron microscopy (SEM), which shows an increase in the amount of $TiO_2$ on the fiber surface, by increasing the overall amount of $TiO_2$. Results indicate the improvement in dye adsorption by increasing the amount of $TiO_2$. This confirms that with increasing the amount of $TiO_2$, these particles are placed among the molecular chains and in this case, the distance among polymer chains in amorphous phase become greater so the diffusion of dye molecules increases in the fabric.

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