EFFECT OF UV IRRADIATION ON MECHANICAL AND MORPHOLOGICAL PROPERTIES OF NATURAL AND SYNTHETIC FABRIC BEFORE AND AFTER NANO-TiO₂ PADDING

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Abstract:

In this study, the effect of UV irradiation on mechanical properties of both natural and synthetic fabrics is investigated. Also the UV degradation of fabrics before and after TiO₂ padding is studied. Cotton is used as natural fabric, and polyester, polypropylene, and polyamide were used as synthetic fabrics. After deposition with TiO₂, prepared samples were irradiated by different dosage of UV light and the changes in fiber surface and the adhesion of nanoparticles is tested. The scanning electron microscopy, elemental analyses of Ti, and other methods were used. In some cases, the effect of stabilization of nanoparticles on fibers by UV light was realized. Reasons of this stabilization are the surface changes of polymer fibers—increase in surface roughness and oxidation of surface.

Keywords:

TiO₂, cotton, polyester, polyamide, polypropylene, fibers

1. Introduction

Photocatalysis is a perspective process in many applications, such as waste water treatment, antibacterial treatments, superhydrophilization, and air decontamination [1–4]. In these processes, we need catalyst such as TiO₂ stabilized on a holder. One of the interesting holders of nanoparticles are porous structures based on textile fibers—these structures have large surface area, are mechanically stable, and have liquids and gases that can easily penetrate through these structures [5].

Very recent studies have discussed the application of nanosized TiO₂ in textile finishing, using the sol–gel technique, to impart effective protection against UV radiation and bacteria, stain resistance, deodorization, as well as self-cleaning because of its photocatalytic activity [6–15].

Using titanium dioxide (TiO₂) or nano-TiO₂ as a catalyst or cocatalyst to improve the crease recovery property has been found to be feasible [16–19]. Titanium dioxide is added as a cocatalyst to enhance the finishing performance and minimize the side effect.

The conditions suitable for the catalyst to work properly are essential. The effect of the size of catalyst, which is known as “size effect,” is an important characteristic for recognizing the fundamental catalytic properties. Ultra-fine catalyst is often more active as compared to larger ones probably because of their high surface area. Therefore, small catalytic particle size can enhance the chemical reactivity.

Stabilization of TiO₂ on the surfaces can be based on sol–gel method [20–24]. Photocatalysis is photochemical reaction. The acceleration of this reaction is escorted by the presence of catalyzer. Photochemical reaction is inviting absorption of

lights by materials whose molecules that absorbed energy are broken up to radicals, ions, or atoms [18]. Basic principle of photocatalysis is the transformation of UV light energy to chemical energy to form radicals and similar unstable chemical structures. The hydroxyl radicals (OH) and superoxide radical anions (O²⁻) are supposed to be the primary oxidizing species in the photocatalytic oxidation processes [16,17]. Useful photocatalysts (such as TiO₂) are effective UV absorbers. [25]

In many papers, we can find lot of techniques on how to stabilize nanoparticles on textile fibers based generally on the application of supporting chemicals to protect the surface of polymeric fibers and increase the adhesion of nanoparticles on fiber surface.

The most important properties of textile treatments are durability and washing fastness. Although the nanoparticles can provide high durability for treated fabrics with respect to conventional materials, many researchers have tried to improve wash fastness by means of some binders and spacers or other methods. In this research work, the effect of UV on mechanical properties of both natural and synthetic fabric before and after TiO₂ padding is investigated. Also the effect of UV on washing fastness of TiO₂ on surface of fabrics is studied.

2. Experimental

2.1. Materials and chemicals

Aeroxide P25 Degussa (nano-TiO₂) that contains 70% anatase and 30% rutile was used in this study. The mean diameter of the used nanoparticles was 21 nm. Experiments were realized on textile samples described in Table 1. These four fabrics

represent the mostly used textiles in clothing industry, and they represent polymers with highest difference from chemical point of view. Cotton is a natural fiber based on cellulose, which in contact with liquid water intensively swells and open its internal structure because its nature is polar and hydrophilic. Other three fibers are synthetic and represent different levels of hydrophilicity: polyamide (PA) is hydrophilic and polypropylene (PP) is extremely hydrophobic. The samples were washed using 1 g l⁻¹ nonionic detergent (Triton X-100 solution from Sigma-Aldrich) and 2 g l⁻¹ of sodium carbonate at 50 °C for 30 min before starting the experiments.

2.2. Deposition of TiO₂ nanoparticles

Nanoparticles of TiO₂ were suspended in water system by ultrasound homogenizer Sonopuls HD 3200 (Bandelin Electronics, Germany). Final concentration of TiO₂ was 10 g l⁻¹.

Photocatalytic nanoparticles of TiO₂ were deposited on fiber surfaces by padding technology. Textile samples were immersed in above-described suspension of TiO₂ nanoparticles, squeezed on padding machine with 70% of wet pickup, and dried. Squeezing was realized on pneumatic padding machine Mathis (Switzerland) at a pressure of 4 kN with a velocity of 1 m/min. Drying of samples was realized in basic drying box at 110 °C for 20 min. Before irradiation, textile samples were protected against undefined UV light.

2.3. UV irradiation

In this research, both nano-TiO₂-treated and untreated samples were UV irradiated for up to 600 min. UV light tubes (4_Philips TL 6W-F6 T5) were used. Intensity of UV light on the sample surface was 40.4 mW cm⁻² of UVA and 4.1 mW cm⁻² of UVB. Textile samples were cooled by air flow during UV irradiation. Water is one of the necessary components of photocatalysis. So observing the humidity of sample during the UV irradiation is necessary. In this study, “wet experiment” (air humidity is 95% and pick up 200% of the weight of textile sample) was used. Water was deposited by spraying of distilled water. Experiments were realized in closed PP box with special holder of textile sample (Fig. 1).

2.4. Characterization methods

Mechanical properties of textile samples were measured on laboratory tensile tester Labtest 2.05. Yarns separated from the fabric were analyzed by the velocity of holder, 250 mm/min. Testing length was 200 mm. Samples were acclimatized before irradiation at relative air humidity of 65%. All presented values are calculated as the average value from the 20 measurements.

Quantity of Ti on textile samples was estimated by X-ray fluorescence (XRF). XRF is based on the emission of characteristic secondary or fluorescent X-rays from a material

Table 1: Description of used textiles

Fabric	Abbreviation	Areal density (g m ⁻²)	Structure	Warp set per 10 cm	Weft set per 10 cm	Fiber diameter (μm)
Cotton	CO	115	Plain wave	280	300	10 (noncircular cross section)
Polyester	PES	120	Plain wave	220	190	22
Polyamide 6	PA6	80	Plain wave	340	260	25
Polypropylene	PP	172	Plain wave	90	90	15 (noncircular cross section)

Figure 1: Description of the experimental arrangement—(1) metal mesh holder of sample, (2) transparent foil, (3) flexible holder, (4) irradiating sample, and (5) polypropylene box

that has been excited by bombarding with high-energy X-rays. Used XRF analyzer “ElvaX” is a desktop energy-dispersive X-ray fluorescence (EDXRF) analyzer spectrometer that does not require liquid nitrogen cooling for storage and use. Surface of samples was visualized by scanning electron microscopy on the instrument Tescan VEGA TS 5130MM after gold layer deposition.

3. Results and discussion

3.1. Tensile strength

The results related to tensile strength of samples under different time of UV exposure are shown in Figs. 2–5. In all cases, we can see similar trend on samples with and without photocatalytic TiO_2 nanoparticles. Explanation of results is complicated because tensile strength is based not only on mechanical strength of fibers but also connected with the friction properties of fibers. The friction properties are influenced by deposition of TiO_2 nanoparticles in textile structure. In case of cotton samples, the results show that the strength of sample with nano- TiO_2 in both dry and wet cases is higher than the sample without TiO_2 . It shows that the existence of titanium dioxide causing the increase in the strength of cotton fabric. In shorter time of UV irradiation, the strength is high in wet condition, but by increasing the time of irradiation, the strength decreases. But the effect of UV irradiation is not significant in both the cases.

For PP fabrics (Fig. 3), the UV irradiation causes the reduction of strength; however, it is not noticeable. The behavior of both TiO_2 treated and untreated PP in wet condition is the same. In dry condition, the existence of nano- TiO_2 causes less reduction in strength.

For polyester sample (Fig. 4), linear decrease in the strength during the UV irradiation is achieved. This dependence was observed on samples with and without nanoparticles of TiO_2 . In both dry and wet situations, this reduction is seen. The existence of nano- TiO_2 causes the reduction of strength in polyester samples. Polyester fibers has compact structure, and during the melt spinning, TiO_2 particles is added for reducing the lustre properties. In this research by adding nano- TiO_2 , the extra amounts of TiO_2 are added, and these extra amounts cause the reduction in strength of the polyester samples.

In the case of PA fibers (Fig. 5), the behavior is similar to that of cotton. By UV irradiation for up to 350 min, the strength increases. By increasing the time of irradiation to more than 500 min, the strength reduces again. It should be mentioned that the strength of PA sample after UV irradiation for 600 min is more than that of the sample before irradiation. It means that UV irradiation in case of PA causes increase in strength. For TiO_2 -treated PA, the existence of TiO_2 causes increase in the strength of sample before UV irradiation as compared with untreated PA. By UV irradiation for up to 350 min, the strength of sample increases. However, by increasing the time of irradiation for more than 350 min, the strength is decreased.

(a)

(b)

Figure 2: Tensile strength of cotton fibers as a function of irradiation time (with and without TiO_2): (a) dry conditions and (b) wet conditions

(a)

(b)

Figure 3: Tensile strength of polypropylene fibers as a function of irradiation time (with and without TiO_2): (a) dry conditions and (b) wet conditions

(a)

(b)

Figure 4: Tensile strenght of polyester fibres as a functon of irradiatrion time (with and without TiO_2): (a) dry conditions and (b) wet conditions

(a)

(b)

Figure 5: Tensile strenght of polyamide fibers as a functon of irradiatrion time (with and without TiO_2): (a) dry conditions and (b) wet conditions

It is seen that by UV irradiation for 600 min, the strength of sample is similar to the sample without irradiation.

For PA sample, it should be mentioned that the hydrophilic nature of fiber helps absorb more amounts of TiO_2 . First in short time of UV irradiation or without irradiation, the strength of the sample increases as compared with the sample without TiO_2 . By increasing the time of irradiation to more than 200 min, the strength of the sample decreases significantly. This reduction in strength is caused by photocatalytic activity of nano- TiO_2 . The presence of nano- TiO_2 helps in the transformation of UV light energy to chemical energy to the form of radicals and similar unstable chemical structures. The hydroxyl radicals ($\text{OH}^\bullet$) and superoxide radical anions ($\text{O}_2^{\bullet-}$) are supposed to be the primary oxidizing species in the photocatalytic oxidation processes. In dry condition, the existence of TiO_2 causes increase in the strength of PA fabrics. The effect of UV and nano- TiO_2 on PA samples is similar to that of cotton. It can be because of the hydrophilic nature of both the samples.

3.2. Elemental analyses, XRF

For quantification of adhesion of TiO_2 nanoparticles to the fiber surface, elemental analysis (XRF) was used. The basic idea was if the adhesion is low, we can remove all TiO_2 nanoparticles by washing.

Both UV-irradiated and nonirradiated samples were washed in nonionic surfactant (5 min, 60°C , 1:100, 2 g l^{-1}) in stirred metal beaker.

The washed samples were analyzed, and the XRF values are compared with the initial results of XRF, and the elimination of Ti from sample in percentage was calculated. Calculated results are shown in Fig. 6.

The results show that without any irradiation, the highest adhesion of nanoparticles is for cotton and the lowest is related to PA fibers.

All synthetic fibers have the similar behavior. UV radiation stabilized the nanoparticles of TiO_2 on fiber surface. This effect is extremely effective on PA, where less amount of TiO_2 is removed from samples after 600 min of UV radiation. In case of cotton, the opposite results were achieved. After UV irradiation, more amounts of TiO_2 are removed from the surface of irradiated fibers. It may be due to the increase in the evenness of cotton fibers after UV irradiation.

3.3. Electron microscopy

Electron microscopy was used for the evaluation of fiber surface—visualization of TiO_2 particles and surface roughness.

Figure 6: Quantity of TiO₂ removed by washing from all used fibers, comparison of original and UV-irradiated samples (90 and 600 min)

On cotton fibers, we can see (Figs. 7 and 8) lots of TiO₂ nanoparticles and the roughness of the cotton fibers is not changed by UV irradiation. After washing UV-irradiated cotton, less amounts of TiO₂ remain on the surface, and these results confirm the achieved results by XRF.

In case of polyester, it is also visible that after UV irradiation, more amounts of nano-TiO₂ is attached on the surface of the fibers (Figs. 9 and 10).

On the surface of PP and PA fibers (Figs. 11–14), we can see relatively low quantity of TiO₂ nanoparticles. It is because of even surface of fibers as compare with cotton and polyester fibers.

After UV irradiation, some pores are created on the surface of fibers . These small roughness increase the adhesion of TiO₂ particles on the surface.

Figure 7: Cotton fibers without UV irradiation: (a) sample without TiO₂, (b) sample with TiO₂ before washing, and (c) sample with TiO₂ after washing

Figure 8: Cotton fibers after 600 min of UV irradiation: (a) sample without TiO₂, (b) sample with TiO₂ before washing, and (c) sample with TiO₂ after washing

Figure 9: Polyester fibers without UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) sample with TiO_2 after washing

Figure 10: Polyester fibers after 600 min of UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) sample with TiO_2 after washing

TiO_2 nanoparticles damaged the surface of fibers. It does not have direct influence on tensile strength of fibers, but influences the friction and the stability of TiO_2 nanoparticles on the surface of fibers. Especially, in the case of PA and PP fibers, we observed an increase in the surface roughness based on the local decomposition of polymer surface by photocatalysis (Fig. 15). This increase in roughness is connected with interesting increase in the stability of TiO_2 nanoparticles on the fiber surface.

4. Conclusions

In this research work, the effect of UV on mechanical properties of both natural and synthetic fabric before and after TiO_2 padding has been investigated. Cotton, PA 6, polyester, and PP fibers were treated by UV light with and without TiO_2 particles. The samples were analyzed by tensile strength measurement, washing tests, elemental analyses, and scanning electron microscopy.

Figure 11: Polyamide fibers without UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) sample with TiO_2 after washing

Figure 12: Polyamide fibers after 600 min of UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) sample with TiO_2 after washing

Figure 13: Polypropylene fibers without UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) with TiO_2 after washing

Figure 14: Polypropylene fibers after 600 min of UV irradiation: (a) sample without TiO_2 , (b) sample with TiO_2 before washing, and (c) sample with TiO_2 after washing

The observed behavior of textile structures can be connected with the basic knowledge of photocatalysis and UV damage of polymers. By irradiation of polymer fibers, the UV light penetrate deeply to the polymer mass (Fig. 15a), and the polymer composition is changed by chemical reaction, and consequently, the mechanical strength of fibers is reduced. By adding nanoparticles of TiO_2 on the surface of fibers, the UV light is effectively absorbed at the surface (Fig. 15b) and the UV light energy is transformed into chemical energy on the fiber surface. This change in UV light flow increases the damage of fiber surface and protects the mass of fiber. If the deposition of

TiO_2 particles is not even on the fiber surface (in some places, the fiber surface will be without TiO_2 nanoparticles), then the mass of polymer is not enough protected against UV light and mechanical properties of fabrics such as tensile strength is decreased. The observed changes in mechanical properties are, in our cases, based on the damage of fibers by UV light and by the change in friction properties of fibers. In case of cotton samples, UV irradiation do not play any role in reducing the strength of samples. Also the existence of nano- TiO_2 causes the strength to increase; however, it is not noticeable. The reason can be because of uneven structure of cotton fibers.

Figure 15: Damage of polymer fiber by UV irradiation (cross section): (a) without TiO_2 and (b) with TiO_2 particles

Acknowledgment

This study was supported by TAČR TA01010613—“Vodné nanodisperze pro funkční povrchové úpravy” (Nanocover), Czech Republic.

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