Development of Self-Cleaning Denim Fabrics

Ş S Uğur¹, A M Sarıuşk², E Çavuşlar¹ and M Ertek³
¹Department of Textile Engineering, Suleyman Demirel University, Isparta, Turkey
²Department of Textile Engineering, Dokuz Eylül University, İzmir, Turkey
³Gap Textile, Çalık Denim Group, Malatya, Turkey

E-mail: suleugur@sdu.edu.tr

Abstract. Denim fabrics coated with TiO₂ nanolayers for self-cleaning properties by using a continuous layer-by-layer method. Nanolayer coated denim fabrics washed with an enzyme process for aging affect. Fabrics were analyzed with SEM-EDX and XPS measurements. Self-cleaning properties of the nanolayer deposited denim fabrics were tested according to red wine stain against to Suntest visible light irradiation after 72 h. And also, some physical (air permeability, tensile strength) and color (color difference and rubbing fastness) properties were evaluated.

1. Introduction
The Layer-by-Layer (LbL) deposition process which is based on the sequential adsorption of oppositely charged colloids (charged molecules, nanoparticles, dyes, proteins and other supramolecular species), has initiated the easy preparation of nano-coated textile materials to be used as functional textiles [1-4]. Denim is constructed in twill weave which included the indigo-dyed warp and white weft yarns. The household laundering treatment of denim fabrics is the important parameters influencing cloth shade and the fabric mechanical properties [5]. To facilitate the natural distressing process, some wearers of dry denim will abstain from washing their jeans for more than six months [6]. The field of self-cleaning coatings is divided into two categories as hydrophobic coating and hydrophilic coating. Hydrophilic coatings chemically break down dirt when exposed to UV light, a process named as photocatalysis. In the present study, an attempt was made to improve self-cleaning properties of denim fabrics by using padding layer-by-layer (LbL) process.

2. Material and Method
Indigo dyed denim fabrics were purchased from GAP Textile and used for obtaining denim fabrics which will gained self-cleaning properties. The cationic indigo dyed denim fabrics were prepared by using two different commercial cationic dye fixing agent (Aysol Mordan T and Ayfix RF). Anatase titanium oxide nanoparticles (particle size <25 nm, specific surface area 200-220 m²/g) was purchased from Aldrich and used for multilayer film composition. 1, 3 and 5 g/l nanoparticle suspensions were prepared at 40 W for 1 h by Sonics Vibra-Cell Ultrasonic Homogenizer. In the deposition process, the cationized and untreated denim fabrics were deposited with 10 multilayer nanoparticle films (table 1). After LbL deposition process, denim fabrics were washed according to an enzyme process.

Scanning electron microscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS) measurements were used to verify the presence of the deposited nanolayers. The self-cleaning properties of the denim fabrics coated with the TiO₂ nanolayers were tested as discoloration of red wine stain against to Suntest visible light irradiation after 72 h [7]. Air permeability, color difference values, rubbing fastness and tensile strength analyses were performed to...
examine the LbL process effect on the cotton textile fabric properties. The LbL deposited nanolayers properties were analyzed after enzyme washing process.

Table 1. Nanolayer deposition encoding system.

| Denim | TiO$_2$ nanoparticle | Cationic agent |
|-------|----------------------|----------------|
| D-T1  | -                    | -              |
| D-T1R | 1 g/l                | Ayfix RF       |
| D-T1M |                      | Mordan T       |
| D-T3  | -                    | -              |
| D-T3R | 3 g/l                | Ayfix RF       |
| D-T3M |                      | Mordan T       |
| D-T5  | -                    | -              |
| D-T5R | 5 g/l                | Ayfix RF       |
| D-T5M |                      | Mordan T       |

3. Results and Discussion
Scanning electron microscopy was used to verify the presence of the deposited nanolayers on multilayer nanoparticle deposited denim fabrics. TiO$_2$ nanoparticles can be clearly seen on the fiber surfaces in the figure 1. The crystalline phase of anatase TiO$_2$ remained unchanged in the resultant TiO$_2$ film coated cotton fibers. With cationization process Titanium element content increases due to the cationic surface charge increases after the process.

|          | SEM images | EDX analysis |
|----------|------------|-------------|
| D        | ![SEM image](image1.png) | ![EDX image](image2.png) |
| D-T5 (Ti: %9.57) | ![SEM image](image3.png) | ![EDX image](image4.png) |
Spectra of 0-1200 eV of denim fabrics coated with TiO$_2$ nanoparticle multilayer films are given in figure 2. The characteristic peaks at energy values of 283.95 and 530.11 eV indicate the content of C and O atoms, respectively, in the core of cellulose. During the TiO$_2$ multilayer film coating process, the titanium (Ti) content formed in the cellulose fibers in the denim fabric is observed with Ti$2p_1$ and Ti$2p_3$ peaks located near the energy value of 460 eV. The relative intensity of Ti peaks increased with increasing concentration. It is also seen that the cationization process performed with Aysol Mordan T is much more effective.
**Figure 2.** XPS analysis of denim fabric untreated and coated with 10-layer nano-TiO₂.

The tensile strength measurements were carried out according to the ASTM 5034-Grab method at the end of the multi-layer coating processes at concentrations 1, 3 and 5 g / l of the TiO₂ 10 layers of denim fabrics and the enzyme washing processes of the coated fabrics. Air permeability tests were carried out at 100 Pa according to the EN ISO 9237 standard. Rubbing fastness were tested according to EN ISO 105-X12 using a Crockmeter. All the test results are given in the table 2.

| Tensile strength After LbL Enzyme washing | Rubbing fastness | Air Permeability (l/m²/s) |
|------------------------------------------|------------------|---------------------------|
| Weft          | 26               | 28 | 61 | 4 | 3 | 114,6 |
| D-T1          | 28               | 60 | 29 | 66 | - | - | 68,4  |
| D-T1M         | 28               | 61 | 30 | 65 | - | - | 58,4  |
| D-T3          | 28               | 60 | 27 | 67 | - | - | 105,6 |
| D-T3R         | 28               | 65 | 26 | 67 | - | - | 75,26 |
| D-T5          | 28               | 60 | 29 | 65 | - | - | 57,5  |
| D-T5R         | 27               | 60 | 27 | 59 | 3 | 3 | 81,8  |
| D-T5M         | 20               | 60 | 27 | 62 | 3 | 3 | 66,28 |

When the air permeability values are examined, the air permeability values of the denim fabrics are reduced as a result of the multilayer coating process performed with TiO₂ nanoparticles. It was observed that the tensile strength values of the denim fabric also increased. As a result of the enzyme washing process, the same strength enhancements continue to show that the coating process is also effective in the washing result. As a result of the multi-layer coating process, the wet and dry rubbing fastness values of the denim fabrics gave the same or better values than the untreated denim fabrics.

LbL coating processes and enzyme washing processes of coated fabrics, color measurements were carried out and the results are given in table 3. As a result of the multilayer coating process carried out with TiO₂ nanoparticles, the L values of the denim fabrics increased. As a result of the multilayer coating process with increasing amount of nanoparticles used in terms of color difference values, it was determined that the value in the denim fabric was increased, but the enzyme washing processes were within acceptable limits below 1 of the color difference values.
Table 3. Color measurement test results of the denim fabric untreated and coated with 10-layer nano-TiO₂.

| Denim | Process type | L   | a   | b    | C    | H    | -    | ΔL | Δa | Δb | ΔC | ΔH | ΔE |
|-------|-------------|-----|-----|------|------|------|------|-----|-----|-----|-----|-----|-----|
| D     | -           | 21.66 | 1.61 | -6.29 | 6.49 | 284.33 | -    |     |     |     |     |     |     |
| Enzyme |            | 21.09 | 1.25 | -7.48 | 7.58 | 279.48 | -    |     |     |     |     |     |     |
| D-T1  | LbL         | 4.70  | -0.80 | -0.75 | 0.60 | -0.92 | 3.92 |     |     |     |     |     |     |
| Enzyme | LbL         | 0.08  | -0.11 | -0.18 | 0.16 | -0.14 | 0.25 |     |     |     |     |     |     |
| D-T3  | LbL         | 12.26 | -1.66 | -0.67 | 0.46 | -1.72 | 9.86 |     |     |     |     |     |     |
| Enzyme | LbL         | 0.15  | -0.16 | -0.48 | 0.45 | -0.23 | 0.54 |     |     |     |     |     |     |
| D-T5  | LbL         | 13.32 | -2.06 | -0.96 | 0.77 | -2.14 | 10.82 |     |     |     |     |     |     |
| Enzyme | LbL         | 0.60  | -0.28 | -0.55 | 0.51 | -0.36 | 0.84 |     |     |     |     |     |     |
| D-T1R | LbL         | 3.56  | -0.73 | -0.44 | 0.29 | -0.80 | 3.01 |     |     |     |     |     |     |
| Enzyme | LbL         | -1.12 | -0.17 | -0.40 | 0.37 | -0.23 | 1.01 |     |     |     |     |     |     |
| D-T3R | LbL         | 5.19  | -1.05 | -0.56 | 0.38 | -1.13 | 4.36 |     |     |     |     |     |     |
| Enzyme | LbL         | -0.66 | -0.25 | -0.64 | 0.60 | -0.34 | 0.90 |     |     |     |     |     |     |
| D-T5R | LbL         | 10.43 | -1.80 | -1.41 | 1.21 | -1.94 | 8.65 |     |     |     |     |     |     |
| Enzyme | LbL         | 0.44  | -0.51 | -1.19 | 1.12 | -0.66 | 1.43 |     |     |     |     |     |     |
| D-T1M | LbL         | 2.03  | -0.28 | -0.17 | 0.10 | -0.32 | 1.64 |     |     |     |     |     |     |
| Enzyme | LbL         | -1.25 | -0.10 | -0.62 | 0.60 | -0.19 | 1.17 |     |     |     |     |     |     |
| D-T3M | LbL         | 7.85  | -1.34 | -0.78 | 0.58 | -1.44 | 6.46 |     |     |     |     |     |     |
| Enzyme | LbL         | -0.25 | -0.27 | -0.48 | 0.43 | -0.33 | 0.65 |     |     |     |     |     |     |
| D-T5M | LbL         | 10.08 | -1.48 | -0.42 | 0.22 | -1.52 | 8.14 |     |     |     |     |     |     |
| Enzyme | LbL         | -0.06 | -0.57 | -0.62 | 0.54 | -0.64 | 1.04 |     |     |     |     |     |     |

There is no standard method for testing the self-cleaning function. As a result of the researches carried out in the literature, it has been determined that the design of the UV cabinet is suitable. For this purpose, a UV cabinet design was carried out in the laboratory and a cabinet design with 3 UV lamps and one fan to reduce the effect of heated air was realized. Taking into consideration the literature studies, as a result of contamination with red wine, TiO₂ coatings of denim fabrics were exposed to UV lights in UV cabinet for 72 hours. Photographs were taken at 4, 8, 24, 48 and 72 hours of denim fabrics and observational analysis was performed. Images of denim fabrics are given in figure 3. Since the multi-layer coated fabric is indigo-dyed and the dark blue color is close to it, it is not possible to perform an accurate observational analysis of the contamination color change and UV light retention results. For this reason, contamination of the indigo dyed denim fabrics has been carried out on the reverse of the usage. When examined in general, it was observed that the color of the wine lacquer was higher in denim fabrics coated with 5 g / l TiO₂.
Figure 3. Self-cleaning test results of denim fabric untreated and coated with nano-TiO$_2$.

4. Conclusion
In conclusion, we have demonstrated the possibility of using LbL process according to padding application both in the laboratory and conventional systems. Denim fabrics coated with the TiO$_2$ nanoparticles exhibit attractive self-cleaning properties especially with the nanoparticle concentration increases.

Acknowledgments

This research is supported by Ministry of Science, Industry and Technology (Republic of Turkey) project number 0645.STZ.2014. Project partner firms is Gap Textile, Calık Denim Group.

References

[1] Decher G 1997 *Science* **277** 1232
[2] Bertrand P, Jonas A, Laschewsky A and Legras R 2000 *Macromol. Rapid Commun.* **21** 319
[3] Uğur Ş S, Saruşık A M and Aktaş A H 2010 *Nanotechnology* **21** 325603
[4] Uğur Ş S and Saruşık A M 2011 *Coloration Technology (Society of Dyers and Colourists)* **127** 372
[5] Khedler F, Dhouib S, Msahli S and Sakli F 2009 *AUTEX Research Journal* **9** 93–100
[6] Sean S 2015 *Heddels.com*. Retrieved (“When Should I Wash My Raw Jeans? – A Rough Guide” 2015-08-25)
[7] Aksit A, Onar N, Ebeoglugil M F, Kayatekin I and Celik E 2007 *AUTEX 2007 (Tampere, Finland)*