# FUNCTIONALIZATION OF COTTON FABRIC WITH

# β-CYCLODEXTRIN AND NANO-ZnO

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This study aimed to evaluate the morphological, thermal, color, and ultraviolet protection properties of 100% cotton fabric treated with β-cyclodextrin (β-CD) and ZnO nanoparticles by the pad-dry-cure technique. The grafting solution was composed of β-CD at 5, 7.5, 10, and 12.5 g/L used alone or in combination with citric acid (2.5 and 5 g/L) as a crosslinking agent, and dibasic sodium phosphate as catalyst (1.5 g/L). The binding of β-CD in cotton was confirmed by the phenolphthalein colorimetric method. The amount of β-CD grafted increased significantly with an increasing concentration used during impregnation. For the fabric samples treated with nano-ZnO, the presence of β-CD imparts a more homogeneous morphology and reduces the total color difference. The use of β-CD was decisive for the UV protection property. Control samples and those functionalized only with ZnO nanoparticles showed minimal protection, but samples containing β-CD and ZnO nanoparticles had very good protection. The results were maintained after five washing cycles at 40 °C, demonstrating the potential of the association of β-CD and ZnO nanoparticles for obtaining functional textiles.

*Keywords*: cotton fabric, ZnO nanoparticles, functional textiles, UV protection

## INTRODUCTION

There has been an increased interest in the textile sector in using nanotechnology to develop nanocomposite textile fibers, nanofibers, and fabrics finished with nanomaterials.[1] These textile products can be designed to withstand high mechanical stress or to provide different functionalities, such as flame retardancy, water and oil repellency, antimicrobial activity, and ultraviolet protection.[2,3] Also, there is an increase in the consumer demand for innovation and products that offer outstanding properties in terms of comfort, safety, and durability of functional effects.

Nanoparticles, such as metallic silver nanoparticles, metallic oxides, carbon nanotubes, and nanoclay, are widely explored to assign such functionalities.[4] Among these, ZnO nanoparticles have great potential for use in textile products due to their antimicrobial, ultraviolet protection, and photocatalytic properties.[5,6] In addition, these nanoparticles are biocompatible, have low toxicity, and are relatively low cost.[7]

The ability of ZnO or other nanoparticles to obtain cotton finishes with antimicrobial and anti-UV functionalities has already been reported.[8–11] However, a significant challenge in developing functional finishes lies in the durability of the effect against successive washing processes. Alternatives, such as plasma modification[12] and *in-situ* synthesis of nanoparticles[13,14] have been evaluated to increase the durability of treated textiles. Processes involving plasma still require high initial investments and can be difficult to upscale. The *in-situ* technique has presented as a disadvantage the lack of control of material formation within the textile matrix.[4]

β-Cyclodextrins (β-CD) represent a promising alternative to overcome limitations regarding treatment durability, as they can effectively bind to cotton and form host-guest interactions with organic and inorganic molecules. Cyclodextrins are cyclic oligosaccharides formed by the enzymatic degradation of starch and are composed of glucose units linked by α-(1→4)-glycosidic bonds.[15] This structure is arranged in a conical trunk shape with a hydrophilic outer surface and a lipophilic inner cavity, which can accommodate several molecules, such as drugs,

dyes, insecticides, essential oils, cosmetics, and other compounds.[16,17]

β-Cyclodextrins can be grafted onto cotton fibers through esterification using polycarboxylic acids, such as citric acid or 1,2,3,4-butane tetra-carboxylic acid (BTCA) as cross-linked agents.[17,18] This reaction forms an ester linkage between the carboxyl groups of the polycarboxylic acid and the hydroxyl groups of cellulose and β-CD. Although the application of ZnO nanoparticles and cyclodextrins is already common in the textile area, the influence of the combined use of these compounds on the properties of a cotton substrate is not known.

Therefore, this study aims to graft β-CD onto cotton fabric using citric acid as crosslinker and load ZnO nanoparticles in different concentrations. Morphology, thermal and ultraviolet protection properties of the cotton fabrics with and without β-CD grafting were compared. To the best of our knowledge, this is the first study on the simultaneous use of β-CD and ZnO nanoparticles for textile applications.

## EXPERIMENTAL
### Materials
Bleached 100%-cotton fabric, with a plane weave (160 g/m$^2$) was used as a textile substrate. To remove residual chemicals, the fabric was washed at 60 °C using non-ionic detergent (1 g/L) for 20 min, rinsed in water at 25 °C, and then oven-dried. β-Cyclodextrin (β-CD) and an aqueous suspension of ZnO nanoparticles (20 wt% and ≤40 nm average particle size) were purchased from Sigma-Aldrich (USA). All other chemicals were analytically pure and were used as received.

### Fabric treatment with β-CD
β-CD was grafted to the cotton fabrics through the pad-dry-cure method. The aqueous solution for the treatment was composed of β-CD (5, 7.5, 10 and 12.5 g/L), citric acid (2.5 and 5 g/L) as a crosslinker, and dibasic sodium phosphate as catalyst (1.5 g/L). In triplicate, cotton fabric samples of 6.45 cm$^2$ were dipped into a 10 mL treatment solution under gentle stirring for 10 min. After soaking, the samples were passed through two roller padders of a Foulard (TC 2060-Texcontrol) at 1.5 bar and 2 m/min to obtain a wet pick-up of around 90%. The samples were dried at 110 °C for 5 minutes and cured at 150 °C for 2 minutes in a laboratory-type steamer (Mathis, DH-E-B). To remove unbound material, the samples were thoroughly rinsed with distilled water and dried at 40 °C.

For fabric functionalization with ZnO nanoparticles, the commercial suspension of nanoparticles was diluted in distilled water to form 1%, 2.5% and 5% (w/v) suspensions, which were dispersed using an ultrasound bath. Cotton fabric samples were immersed in 10 mL of the ZnO suspension following the pad-dry-cure procedure already described. Samples treated with β-CD and ZnO were obtained by immersing the samples in a ZnO suspension containing 10 g/L of β-CD, 2.5 g/L of citric acid, and 1.5 g/L of catalyst.

### β-CD quantification
The amount of β-CD grafted onto cotton fabric was quantified by the phenolphthalein method, according to Cebrales *et al.*[19] This method is based on the formation of 1:1 complexes between β-CD and phenolphthalein, which decreases the absorbance of the alkaline phenolphthalein solution. First, a phenolphthalein solution at 4 mM was prepared in ethanol. Then, 2 mL of this solution was added to 200 mL of aqueous sodium carbonate solution containing 8 mL of ethanol. The samples previously treated with β-CD were immersed in 10 mL aliquots of this final alkaline solution for 30 minutes under magnetic stirring. After the immersion period, an aliquot of the solution was taken, and the absorbance was measured by UV-vis spectrophotometry (Micronal AJX-1900) at 553 nm. Measurements were performed in triplicate with independent samples.

### Morphology
The morphology of the cotton fabrics before and after the treatments with β-CD and ZnO nanoparticles was evaluated by scanning electron microscopy (SEM). Before the analysis, the samples were fixed with carbon tape on the stubs and covered with a thin layer of gold using Leica metalizing equipment (model EM SCD 500) to obtain the necessary conductivity. The samples were then analyzed in a JEOL microscope (model JSM-6390 LV), at an accelerating voltage of 10 kV.

### Color measurements
Color parameters and the whiteness degree of the treated and untreated samples were performed on a DATACOLOR 500 spectrophotometer, using the CIE L*a*b* color space at D65/10°. In this system, L* is the color lightness (L* = 0 for black and L* = 100 for white), a* is the green (-)/red (+) axis, and b* is the blue (-) /yellow (+) axis.

The measurements were taken at three different points of each fabric face using a 6 mm aperture. The total color difference (ΔE*), calculated by Equation 1, was used to compare untreated (control) and fabrics treated with β-CD and β-CD-ZnO:

$$\Delta E = ( \Delta L^2 + \Delta a^2 + \Delta b^2 )^{1/2}$$
(1)

where ΔL*, Δa*, and Δb* are the difference between the L*, a*, and b* values, respectively, of the cotton fabric before and after the treatment.

**Ultraviolet protection factor (UPF)**

The UPF of the cotton samples was measured according to the Australian/New Zealand Standard AS/NZS 4399:2017, with a Cary 100 UV-vis spectrophotometer from Agilent Technologies. The transmission of ultraviolet radiation through the samples was measured in the spectral range between 290 and 400 nm.

**Statistical analysis**

To evaluate statistically significant differences ($p < 0.05$) among the averages, the analysis of variance and Tukey's test were conducted with Statistica software version 7.0.

## RESULTS AND DISCUSSION
### β-CD quantification

The amount of β-CD grafted on cotton fabrics was quantified by the phenolphthalein method, which is based on the formation of β-CD/phenolphthalein inclusion complexes in alkaline media.[19] While phenolphthalein in the free form has an intense pink color, the complexed form (1:1) is colorless. Therefore, the greater availability of β-CD cavities for the formation of inclusion complexes results in absorbance reduction of the phenolphthalein

solution. The results obtained are shown in Table 1.

Comparing the amount of β-CD data in the samples after impregnation and after washing indicates a significant reduction for all treatments. This confirms that most of the β-CD used in the treatment was physically deposited on the fabric, but grafting also occurs, given the retention after washing.

The presence of the crosslinker and the catalyst did not significantly increase the amount of β-CD impregnated. Citric acid (CA) was selected as crosslinking agent, because it is a polycarboxylic acid much more accessible and less toxic than 1,2,3,4-tetracarboxylic acid butane (BTCA), commonly used for β-CD grafting in cotton.[20] However, the investigation of its potential as a crosslinker is limited to a few studies with quantification of grafting by the gravimetric method.[21,22] As the reactivity of the OH groups of β-CD and cellulose is similar, β-CD–CA–cellulose and cellulose–CA–cellulose compounds can be formed. Therefore, the mass gain could indicate both β-CD grafting and crosslinking of the cellulose groups by the citric acid.

Table 1
Quantification of β-CD impregnated (before washing) and grafted (after washing) on cotton fabric

| β-CD (g/L) | Crosslinker (g/L) | Catalyst (g/L) | β-CD impregnated (mmol/g)* | β-CD grafted (mmol/g)** |
|---|---|---|---|---|
| 5 | 0 | 0 | $0.63 \pm 0.002$ ef | $0.14 \pm 0.079$ gf |
| 5 | 2.5 | 1.5 | $0.59 \pm 0.021$ f | $0.11 \pm 0.028$ f |
| 5 | 5 | 1.5 | $0.63 \pm 0.075$ ef | $0.063 \pm 0.014$ g |
| 7.5 | 0 | 0 | $0.94 \pm 0.009$ d | $0.34 \pm 0.036$ de |
| 7.5 | 2.5 | 1.5 | $0.88 \pm 0.027$ d | $0.25 \pm 0.051$ ef |
| 7.5 | 5 | 1.5 | $0.74 \pm 0.014$ e | $0.24 \pm 0.018$ f |
| 10 | 0 | 0 | $1.09 \pm 0.020$ c | $0.46 \pm 0.022$ ab |
| 10 | 2.5 | 1.5 | $1.08 \pm 0.051$ c | $0.38 \pm 0.015$ bcd |
| 10 | 5 | 1.5 | $1.13 \pm 0.002$ c | $0.37 \pm 0.021$ cd |
| 12.5 | 0 | 0 | $1.23 \pm 0.002$ ab | $0.50 \pm 0.018$ a |
| 12.5 | 2.5 | 1.5 | $1.32 \pm 0.004$ a | $0.48 \pm 0.015$ ab |
| 12.5 | 5 | 1.5 | $1.26 \pm 0.002$ ab | $0.45 \pm 0.019$ abc |

*Determined after the impregnation process of Foulard, **Determined after washing for the removal of unbonded β-CD; Averages with the same subscript letter in the same column had no significant differences ($p < 0.05$) according to Tukey's test

In the present study, the fact that the crosslinker did not increase the amount of β-CD grafted may be related to a preferential formation of cellulose–CA–cellulose or β-CD–CA–β-CD compounds induced by the reaction conditions. In addition to the concentrations of the reagents, parameters such as reaction time and temperature

must be considered to ensure a greater degree of cyclodextrin grafting onto the cotton fiber.

Significant differences in the amount of cyclodextrin grafted in the samples were observed with increasing concentration of β-CD in the treatments. For the lowest concentration of β-CD (5 g/L), about 80% of the impregnated amount

was removed after washing. The percentage removed at the highest concentration (12.5 g/L) was around 60%. This behavior was also observed by Abdel-Halim *et al*.,[20] who evaluated β-CD grafting on cotton using BTCA as a crosslinker and sodium hydrophosphite as a catalyst. The authors attributed the smaller graft in the lower concentrations of β-CD to the dilution effect, since the molecules are in lesser quantity around the fabric and the crosslinker molecules. At higher concentrations, more β-CD molecules will be near the fabric for the binding.

For the cotton fabrics with nano-ZnO treatment, the CD concentration of 10 g/L, with 2.5 g/L citric acid and 1.5 g/L catalyst was selected.

**Morphology**

Figure 1 shows the SEM images of the control fabric and fabric treated with β-CD and nano-ZnO.

The images of the control sample show a smooth and uniform structure, with the typical flattened appearance of the cotton fibers, as well as the presence of convolutions and twists along the length.[23] The treatment with β-CD did not change the fiber morphology.

Compared to the SEM images of the control and β-CD-treated fabrics, the presence of ZnO nanoparticles on the fiber surface is clearly distinguished. The micrographs reveal an increase in heterogeneity and the presence of agglomerates with increasing ZnO concentration.

In the images of the samples treated with β-CD and ZnO, the distribution of material on the fibers, especially in concentrations of 2.5% and 5% of ZnO, is much more homogeneous, with less roughness and agglomeration. This result may be correlated to the β-CD grafting on the cellulose fibers and the concomitant process of complexation with the ZnO nanoparticles. Chemical interactions between CDs and cellulose and the accommodation of nanoparticles in the inclusion complexes may have provided a better distribution of these on the cotton fiber.

Although the nanoparticles are dispersed on the fiber surface in both cases (with and without β-CD), it is reasonable to expect that larger agglomerates will be more easily removed from the fiber surface after washing, while smaller particles will be able to penetrate deeper and adhere strongly to the tissue structure. Macroscopically, the treatments of the cotton fabric did not alter the characteristics of softness and smoothness to the touch.
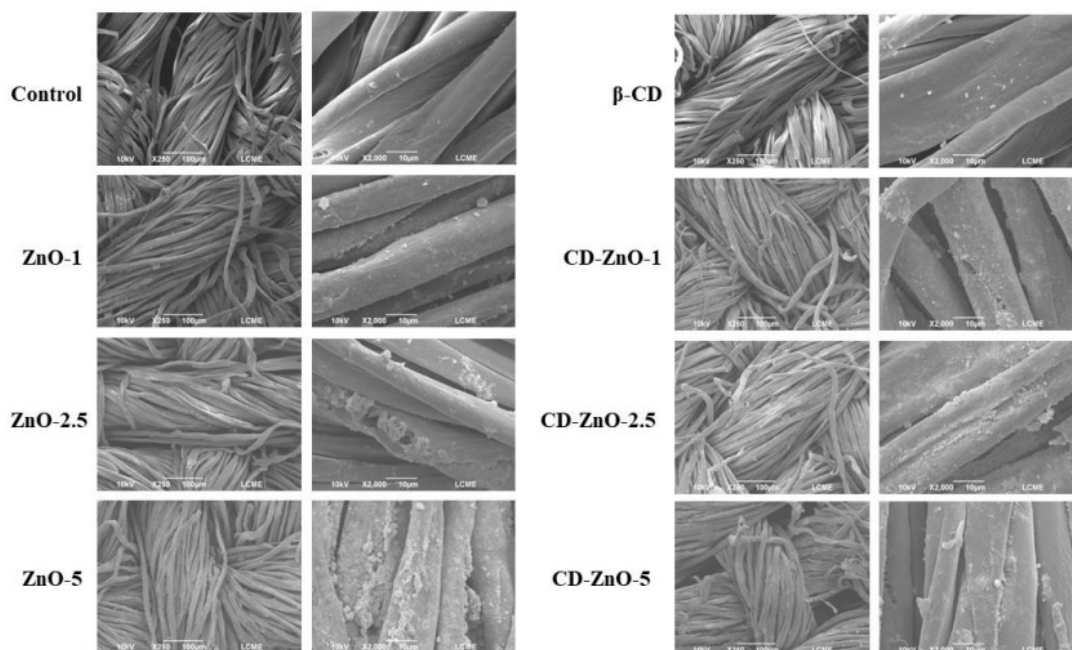


Figure 1: SEM images of untreated (control) and treated cotton fabric samples

Table 2
Measured CIELAB color values (L*, a*, b*) and calculated total color difference (ΔE)
of the cotton fabric samples

| Sample | L* | a* | b* | ΔE |
|---|---|---|---|---|
| Control | 97.16 ± 0.09 [ab] | 5.18 ± 0.11 [a] | -18.36 ± 0.21 [e] | - |
| CD | 97.43 ± 0.10 [a] | 3.17 ± 0.11 [c] | -14.93 ± 0.16 [d] | 3.75 ± 0.16 [d] |
| ZnO-1 | 96.96 ± 0.14 [abc] | 3.00 ± 0.30 [c] | -11.65 ± 0.09 [b] | 6.80 ± 0.08 [b] |
| ZnO-2.5 | 96.70 ± 0.11 [bc] | 2.19 ± 0.16 [d] | -8.41 ± 0.46 [a] | 10.16 ± 0.49 [a] |
| ZnO-5 | 96.54 ± 0.08 [c] | 1.92 ± 0.11 [d] | -7.33 ± 0.34 [a] | 11.28 ± 0.35 [a] |
| CD-ZnO-1 | 96.58 ± 0.37 [c] | 3.78 ± 0.12 [c] | -13.26 ± 0.30 [c] | 5.10 ± 0.34 [c] |
| CD-ZnO-2.5 | 96.73 ± 0.25 [bc] | 3.15 ± 0.19 [d] | -11.23 ± 0.69 [b] | 7.19 ± 0.73 [b] |
| CD-ZnO-5 | 96.53 ± 0.08 [c] | 2.06 ± 0.07 [d] | -7.59 ± 0.33 [a] | 10.99 ± 0.33 [a] |

Averages with the same subscript letter in the same column had no significant differences ($p < 0.05$) according to
Tukey's test

## Color properties

Table 2 shows the values obtained for each of the parameters of the CIELab system (L*, a*, b*) and the result obtained for the total color difference (ΔE).

The values of the luminosity parameter (L*) were close to 100 (+ light), which is expected since the samples are white. Compared with the control sample, the functionalization with ZnO, both in the absence and in the presence of β-CD, had little influence on this parameter.

The parameters a* and b* were significantly reduced with the treatment with β-CD (sample CD) and with the increased concentration of ZnO in the samples. The reduction in the a* parameter, which indicates that the color tends from red to green, was greater for ZnO concentrations of 2.5% and 5%, with no significant difference between samples with and without β-CD.

The b* parameter, whose reduction indicates that the color tends from blue to yellow, had greater reductions in samples without β-CD. The value of the parameter b* for the control sample indicates that it has a bluish tendency, which can be correlated with the optical brighteners. These substances are used to enhance and maintain the desired whiteness effect of colorless textile materials by absorbing light in the ultraviolet region (340–380 nm) of the electromagnetic spectrum and re-emitting light in the blue region (425–450 nm) of the visible spectrum.[24] The human eye perceives slightly bluish materials to have a more uniform and, therefore, lighter spectral distribution. As cotton tends to have a yellowish hue, which can be associated with poor product quality, the textile industry often uses bleaches to create the whitest appearance.

The data also indicate that the reduction of the parameter b* was lower for the samples that received treatment with β-CD, being significant in the concentrations of 1% and 2.5% of ZnO. This behavior may be associated with the formation of β-CD inclusion complexes with ZnO, allowing a more homogeneous distribution over the grafted fiber.

The total color difference (ΔE) was calculated using the control sample as a reference. The difference increased significantly with increasing ZnO concentration, being higher for samples that did not receive β-CD treatment. This result corroborates the SEM images, which showed greater roughness and deposition of aggregate material in samples with higher concentrations of ZnO and without β-CD.

The influence of sample treatments on the whiteness degree was also evaluated and the results are shown in Figure 2. The same trend of the color results was observed with a reduction of whiteness with the application of β-CD and with increasing concentrations of ZnO. The comparison of the results for the samples with ZnO indicates that the presence of β-CD contributes to the maintenance of the whiteness degree, which may be associated with better distribution over the fiber, as observed in the SEM.

The reflectance curves in Figure 3 confirm that the cotton fabric has optical brightener due to percentages greater than 100% in the blue region (425–450 nm) and that this effect was reduced with treatment with β-CD and with increasing concentrations of ZnO. The curves of all the samples in this specific region showed that the reduction occurred in the following order: CD < CD-ZnO-1 < CD-ZnO-2.5 < ZnO-1 < ZnO- 2.5 <

CD-ZnO-5 < ZnO-5. These results corroborate the trend observed in the total color difference and the degree of whiteness.

**Thermal analysis**

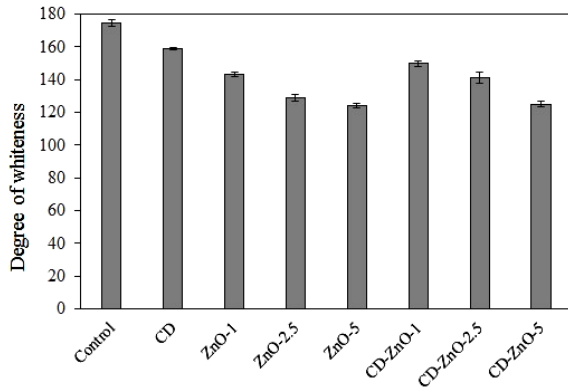The comparative thermal behavior of different cotton fabric samples (control, grafted with β-CD, treated with ZnO-5, and with β-CD-ZnO-5) in a nitrogen atmosphere is shown in Figure 4 and the main information about the thermal events is tabulated in Table 3. Samples ZnO-1 and ZnO-2.5 presented similar behavior to ZnO-5, as well as samples β-CD-ZnO-1 and β-CD-ZnO-2.5 were similar to β-CD-ZnO-5. Therefore, these data were not shown.



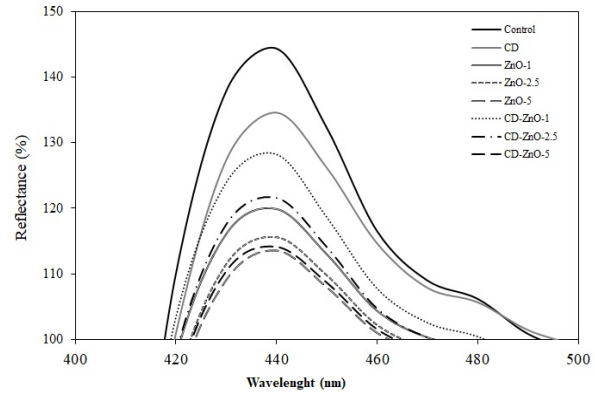Figure 2: Degree of whiteness of untreated (control) and treated cotton fabric samples



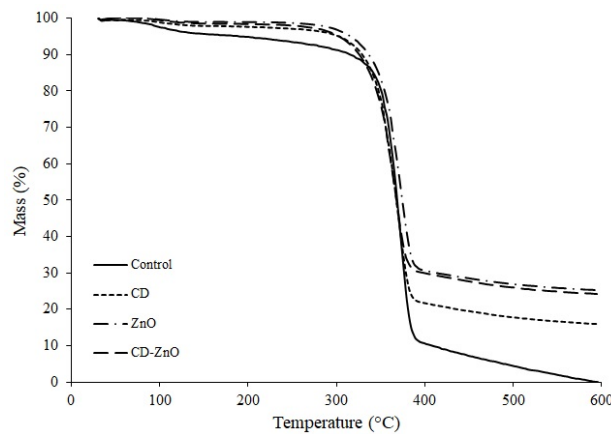Figure 3: Reflectance curves of untreated (control) and treated cotton fabric samples



Figure 4: TGA curves for untreated (control) and cotton fabric samples treated with β-CD, ZnO nanoparticles and β-CD-ZnO

Table 3
Thermogravimetric data of mass loss, decomposition temperatures and residue for different samples of cotton fabric

| Sample | Mass loss at 100 °C (%) | T degradation (°C) | T max (°C) | Mass loss at 400 °C (%) | Residue at 600 °C (%) |
|---|---|---|---|---|---|
| Control | 2.42 | 292−400 | 369 | 89.26 | 0.13 |
| CD | 1.07 | 277−401 | 366 | 78.22 | 15.86 |
| ZnO | 0.26 | 259−406 | 371 | 69.55 | 25.32 |
| CD-ZnO | 0.67 | 254−400 | 368 | 70.09 | 24.09 |

Cellulose fiber degradation includes three steps: initial decomposition (volatilization), principal decomposition, and carbonization.[25] The initial stage occurs below 200 °C, with low mass loss due to the evaporation of adsorbed water and dehydration of anhydroglucopyranose chain segments.[25,26] The water molecules absorbed superficially by the cotton fabric will evaporate at

temperatures below 100 °C. In contrast, the water molecules that have interacted with the -OH functional groups in the cotton will evaporate at higher temperatures.[14] The mass loss at a temperature of 100 °C (Table 3) is less than 3% and is reduced with the presence of β-CD and ZnO.

TGA curves indicate rapid and significant mass loss between 250 and 400 °C, with each sample exhibiting a similar profile in thermal degradation. In this main degradation step, most of the pyrolysis products are formed due to the depolymerization of cellulose, with the breaking of the glycosidic bonds and subsequent breaks of the glucose molecule.[25] The temperature at which the maximum loss rate occurred ranged between 366 °C and 371 °C (Table 3), with degradation starting at approximately 250 °C for the sample treated with β-CD-ZnO. This information is relevant for cotton processing. The maximum temperature to which the cotton samples were subjected during the pad-dry-cure processing was 150 °C in the fixation step, below the temperature at which the material starts to degrade. The minimal differences in the temperatures of the maximum decomposition rate agree with that reported by Román et al.[14] for the treatment of cotton fabric with ZnO nanoparticles.

Although the temperature of the main degradation step was similar, the mass loss was different for the samples. At 400 °C, the mass loss was 89.3% and 78.2% for the control and β-CD grafted sample, respectively. The samples with ZnO and β-CD-ZnO lost 69.5% and 70.1% of their initial masses, respectively. These results indicate that the presence of β-CD and ZnO can reduce the cotton fabric's thermal degradation rate, delaying the reactions that result in L-glucose.

Above 400 °C, carbonization of cellulose occurs, and dehydration and carbonization reactions lead to the production of glucose, water, and carbon oxides.[26] For the control sample, the mass loss reached almost zero, generating a carbonaceous residue of only 0.13%. The residue increased to 15.86% in the presence of β-CD, and to about 25% for samples containing ZnO (Table 3).

According to Cabrales et al.,[19] the greater the amount of grafted cyclodextrin, the greater the residual mass obtained by thermogravimetric analysis. Such an effect would be due to the reaction between the residue of the cyclodextrin degradation with the cellulose, causing the generation of volatile products to be smaller and, consequently, the residual mass to be larger. This behavior, therefore, confirms the presence of β-CD in the cotton sample.

The residue at 600 °C of the samples containing ZnO nanoparticles was higher than for the control and for the samples grafted with β-CD. Studies related to the flame retardancy of cotton fabrics have shown that ZnO nanoparticles are adequate for forming carbonaceous residue, reducing flammability.[27-29] According to Tawiah et al.,[30] the carbonaceous residue acts as a physical barrier that reduces the physical contact between the flame and the unburned cotton fabric, eventually preventing the rest of the fabric from burning. This result is very interesting, as it points to the potential of ZnO nanoparticles to increase the thermal stability of cotton fibers at high temperatures.

**UV protection**

The UPF evaluation was performed for the untreated sample (control), for samples treated with 2.5% ZnO (ZnO-2.5), and samples grafted with β-CD and treated with 2.5% ZnO (CD-ZnO-2.5). Due to technical limitations, only one concentration of ZnO could be evaluated, and thus an intermediate concentration of 2.5% was chosen.

Table 4
Transmittance (T) and UPF rating for the different samples of cotton fabric

| Sample | T UVA (%) | T (UVB) (%) | UPF |
|---|---|---|---|
| Control | 9.22 | 15.41 | 6 ± 1 |
| ZnO | 6.36 | 7.78 | 13 ± 1 |
| CD-ZnO | 2.56 | 2.01 | 50 ± 10 |
| ZnO-1 washing | 6.32 | 7.50 | 13 ± 1 |
| ZnO-5 washings | 6.96 | 9.23 | 11 ± 1 |
| CD-ZnO-1 washing | 2.39 | 1.84 | 54 ± 7 |
| CD-ZnO-5 washings | 2.89 | 2.28 | 43 ± 3 |

To evaluate the durability of the functionalization, the UPF was also evaluated after the samples were subjected to 1 and 5 washing cycles. The results are shown in Table 4.

The results obtained show that β-CD played a crucial role in increasing protection against ultraviolet radiation. Compared with the control sample, the treatment with ZnO increased the UPF twice and grafting with β-CD increased the UPF value by 17.5 times. In terms of classification, the treatment with ZnO only is not sufficient to impart minimal protection classification according to AS/NZS 4399:2017 (15 < UPF < 29). The samples grafted with β-CD and treated with ZnO showed very good protection score (30 < UPF < 49). These results suggested that the CD-ZnO-treated cotton is effective at blocking out ultraviolet light and providing very good protection to human skin.

As observed in the SEM images, the deposition of ZnO in the fibers grafted with β-CD is more uniform and presents fewer clustered regions, compared to fibers without β-CD. The UPF result reinforces the hypothesis of the formation of a ZnO inclusion complex in β-CD, which contributes to the dispersion of nanoparticles in the fiber.

The protective effect against UV radiation of ZnO nanoparticles has been demonstrated in several studies, but the UPF value depends on the particle size and the deposited amount. For Saravanan,[31] ZnO nanoparticles with uniform size distribution (20-40 nm) and minimum concentration can result in higher levels of UV blocking. Yadav *et al.*[32] observed the influence of ZnO particle size on UV radiation absorption. It was observed that the absorption in cotton fabric coated with 2% ZnO nanoparticles at 40 nm was 75% higher than in conventional-size ZnO-coated fabric. Noman *et al.*,[33] used an *in situ* ultrasonic acoustic method to synthesize and anchor ZnO nanoparticles on a cotton fabric surface. Untreated samples presented a UPF of 2 and samples treated with ZnO nanoparticles showed a UPF between 74 and 216, with lower values for smaller amounts deposited.

The results for the samples submitted to a washing cycle indicate that there was no loss of functionalization.

## CONCLUSION

β-CD was successfully grafted onto 100% cotton fabrics by the pad-dry-cure method. The grafting was confirmed by the phenolphthalein colorimetric method, and it was observed that the grafted amount increased with the increase in the β-CD concentration, but it was not influenced by the crosslinker and the catalyst. Different concentrations of ZnO nanoparticles resulted in the presence of particulate material on the fibers and increased roughness, while in the presence of β-CD, the fibers presented a more homogeneous surface, suggesting the formation of inclusion complexes. Increasing concentrations of ZnO nanoparticles significantly reduced the colorimetric parameters and, consequently, the total color difference. Compared to samples functionalized with ZnO alone, samples treated with β-CD resulted in a smaller total color difference. Thermal analyses indicated that ZnO treatment contributes to increasing the thermal stability of cotton fabric. β-CD played a crucial role in the UV protection property of the samples, imparting a "very good" UPF rating for the cotton fabric, which was maintained after 5 washing cycles.

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