Assessment of UV Protection Factor of Flax, Polyester and Nylon Fabrics Treated with Zinc oxide Nanoparticles

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ABSTRACT

In this study, influence of nano-zinc oxide treatment on the UV protection properties of the widely used apparel fabrics including flax, polyester, and nylon, were investigated by means of ultraviolet protection factor (UPF) assessment. Nanoparticle content of the flax, polyester, and nylon fabrics were determined to be 1.2, 0.9, and 1.5 wt%, respectively. The UPFs of non-treated fabrics were in the range of 1.5 to 2.2 in the entire UV region. An improvement in UPF was obtained after introducing the nanoparticles into the fabrics. Approximately a sixfold-increase in UPF (11.02 ± 1.57) against UV-B was recorded for nylon. Flax and polyester fabrics had nearly the same UPF values around 2.8 against UV-B, while they were close to each other (2.71 ± 0.22 and 2.61 ± 0.28 for flax and polyester, respectively) against UV-A. SEM micrographs showed that nanoparticles agglomerated on flax and polyester in high extent, whereas they existed as dispersed particles at micro scale together with some slight agglomeration inside nylon.

Keywords: Zinc oxide nanoparticle, Textile fabrics, Ultraviolet protection factor

Çinko oksit Nanopartiküllerle İşlem Görmüş Keten, Polyester ve Naylon Kumaşlarının Ultraviyole Koruma Faktörünün Değerlendirilmesi

ÖZET

Bu çalışmada, nano-çinko oksit ile işlem görmüş keten, polyester ve naylon gibi, yaygın olarak kullanılan giyim kumaşlarının UV koruma özelliklerine etkisi ultraviyole koruma faktörü (UPF) değerlendirilmesi ile araştırılmıştır. Keten, polyester ve naylon kumaşların nanopartikül içeriği sırasıyla ağrılık %1,2, 0,9 ve 1,5 olarak belirlenmiştir. İşlem görmemiş kumaşların UPFleri, UV bölgesinde 1,5 ila 2,2 hesaplanmıştır. Nanopartiküllerin kumaşlara daldırılmasından sonra UPF değerinde artış yaklaşık olmuştur. Naylon için UV-B'ye karşı UPF'de yaklaşık altı kat artış (11.02 ± 1.57) bulunmaktadır. Keten ve polyester kumaşlar UV-B'ye karşı 2,8 civarında, hemen hemen aynı UPF değerlerine sahipken; UV-A'ya karşı birbirlerine yakın (keten ve polyester için sırasıyla 2,71 ± 0,22 ve 2,61 ± 0,28) UPF değerleri çıkmıştır. SEM mikrografları, nanopartiküllerin keten ve polyester üzerinde yüksek oranda aglomere olduğunu, ancak naylon içinde yer yer aglomerasyona birlikte genel olarak mikro seviyede partiküler halinde dağılıdığını göstermiştir.

Anahtar Kelimeler: Çinko oksit nanopartikül, Tekstil kumaşları, Ultraviyole koruma faktörü
UV protection has been an important issue for the human health as well as the textile fabrics against the hazardous radiation of UV considering the depletion of ozone layer in the earth’s atmosphere. There are basically two types of ultraviolet radiation (UVR) which are UV-A (400–315 nm) and UV-B (315–290 nm) that can pass through the ozone layer and reach to the earth’s surface. Having a considerably higher energy than the visible light, UVR can cause significant damage in skin and deteriorate the fibers of the textile fabrics [1], [2] Skin cancer is considered to be the most serious long-term health effect of the UVR [3]. UV-proof textiles for apparels in the marketplace has been a growing demand in the society.

There are various factors that play important role in determining the UV-blocking properties of textile fabrics such as fabric composition (made by synthetic and natural fibers or their combinations), construction (weave or knitting which determine the porosity), thickness, dyeing, color, etc. In general, lower porosity, higher thickness, increased weight per unit area regardless of the fabric composition, dyeing, and dark color provide better protection from UVR [4]–[7]. Hence, treating textile fabrics with some chemical formulations to reduce the risk of UVR exposure has been an important task.

In recent years, advances in nanotechnology have opened new frontiers in many fields including textile finishing. Nanoparticles, which offer high durability, biocompatibility, transparency, non-toxicity, have been incorporated into consumer products, such as sunscreens, cosmetics, packagings, as well as textiles finishing including medical fabrics [8]–[11]. Zinc oxide possess a wide direct band gap (3.37 eV), absorb in the UV range, show no degradation under UVR, are inexpensive, transparent, rather stable and considered to be non-toxic and thus they are of paramount importance to study the UV-blocking properties in textile fabrics for apparels [8], [12]–[16].

Zinc oxide nanoparticles (ZnO NPs), as a class of inorganic UV absorber, are superior to commercially available organic UV absorbers, which do not have enough resistance to degradation under UVR exposure, due to the aforementioned advantages [15], [17], [18]. Their UVR protection primarily depends on absorption of UV light and ability to transform it into harmless thermal energy via a photophysical process [16], [19]. Furthermore, UV-blocking ability of ZnO NPs is significantly altered by their size and morphology since unique physico-chemical properties arise at nanoscale due to large surface area-to-volume ratio. Apparently, morphology, size distribution and aggregation behavior of these nanoparticles on the treated textile fabrics influence the overall UV-blocking property [8], [20], [21]. With these unique characteristics, ZnO NPs still have the popularity in UV protection strategies.

There has been several studies in the literature with regard to improve UV protection of textile fabrics such as cotton, polyester/cotton, bleached cotton with or without some extra modifications in the presence of ZnO NPs which are prepared through wet chemical synthesis, sol gel technique or received as powders from commercial sources. Consequently, improved UV-blocking properties are pointed out with different efficiencies of ultraviolet protection factor (UPF) for fabrics treated with ZnO NPs [8], [11]–[14]. UPF is a key parameter, like the sun protection factor for sunscreens, to evaluate the degree of UV-blocking properties of textiles and clothing from UV radiation. UPF value increases as the fabrics’ UV-blocking property is improved [2]. UPF ratings can be found on a special label for textiles finishing and seasonal fabrics.

In this study, it is aimed to assess the degree of UVR protection provided by ZnO NPs impregnated into the three textile fabrics: flax, polyester, and nylon. The chosen apparel fabrics are widely used worldwide in clothing in the marketplace. UPFs of flax, polyester, and nylon fabrics with variable
ZnO NP content were determined using spectrophotometric method. Absorbance data were recorded for both treated fabrics and non-treated ones for control. UPF was determined using the transmittance values of the samples. Morphology, structural details of the synthesized nanoparticles impregnated into the fabrics were investigated through scanning electron microscopy (SEM). Improvements in UVR protection were determined by comparing the results with that of control fabrics which were not treated with any ZnO NPs.

II. MATERIALS AND METHODS

A. SYNTHESIS OF ZnO NPs

In this study, wet chemical method was employed to synthesize ZnO NPs following a procedure reported in the literature [8], [22]. Accordingly, 5.5 g ZnCl₂ (> 98%, sigma-aldrich) was dissolved in 200 mL of deionized water at 90 °C placed in an oil bath. Then, 16 mL 5 M NaOH (ACS reagent, > 97%, pellets from sigma-aldrich) was added dropwise to the zinc chloride solution for 3.5 min under continuous stirring. The mixture was then left to stir for 10 min. Next, the white particles were separated by discarding the supernatant. The remaining concentrated suspension was washed with excess amount of deionized water (1:10 ratio) five times, and the supernatant was discarded each time after washing. The presence of formed NaCl in the product was checked by adding AgNO₃ to ensure all NaCl has been removed from the product. Then, the obtained precipitate was dispersed in 2-propanol (from isolab) and ultrasonicated for 20 min in order to get readily dispersed particles. This was done to disrupt aggregates which particles tend to form at nanoscale. The particles were then collected in the precipitate form by centrifugation at 4000 rpm for 5 min. This step is repeated for three times to get a pure product. Then, the precipitate was heat treated at 250 °C for 5 h to obtain ZnO NPs. FTIR spectroscopy (NICOLET iS5, Thermo Fisher Scientific, Waltham, MA, USA) was used to characterize the chemical structure of the ZnO NPs. The spectra were recorded in the range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹ and 16 scans. Morphology and structural properties of the as prepared nanoparticles were characterized by scanning electron microscopy (SEM). SEM measurements were conducted on a Carl Zeiss Ultra Plus Gemini FESEM scanning electron microscope, at accelerating voltage in the range of 5–10 kV, equipped with an energy dispersive X-ray (EDX) spectrometer. EDX spectroscopy was conducted to identify the elemental composition of the nanoparticles. All tested samples were coated with a thin layer of gold prior to analysis to avoid charging during the interaction of irradiated electrons with the investigated sample.

B. TREATING FABRICS WITH ZnO NPs

Three types of fabrics, namely flax, polyester, and nylon with woven structures were used to study UV protection behavior with ZnO NPs. The fabrics were provided from a local clothing store and they were washed and dried prior to use. Firstly, fabrics were cut into 5×5 cm pieces and weighed. Secondly, ZnO NP dispersion (5 wt%) in 2-propanol was prepared for each tested fabric. Each fabric was immersed in nanoparticle dispersion so that they got wet, and gently shaken for 10 min. at room temperature. Thirdly, ZnO NP-treated fabrics were dried at 130 °C for 15 min.

C. DETERMINING THE UPFs OF THE TESTED FABRICS

UV-blocking property of the tested fabrics was estimated by means of UPF. It is defined as the ratio of the average effective UVR irradiance for unprotected skin (E_eff) to the average effective UVR
irradiance for the skin when it is protected by the test fabric \((E')\) [23] as shown in the following equation.

\[
UPF = \frac{\sum_{290}^{400} E_{\lambda} S_{\lambda} \Delta_{\lambda}}{\sum_{290}^{400} S_{\lambda} T_{\lambda} \Delta_{\lambda}}
\]

(1)

Where, \(E_{\lambda}\) is relative erythemal spectral effectiveness, \(S_{\lambda}\) is the solar spectral irradiance, \(T_{\lambda}\) is the spectral transmittance of each tested fabrics, and \(\Delta_{\lambda}\) is the wavelength step [24]. A classification category of UPF for fabrics was established by the Australian/New Zealand Standard which is accepted as the most widely adopted one for the evaluation and classification of fabrics according to their sun protective properties as given in Table 1 [24].

<table>
<thead>
<tr>
<th>UPF range</th>
<th>UVR Protection category</th>
<th>Effective UVR transmission, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 to 24</td>
<td>Good protection</td>
<td>6.7 to 4.2</td>
</tr>
<tr>
<td>25 to 39</td>
<td>Very Good protection</td>
<td>4.1 to 2.6</td>
</tr>
<tr>
<td>40 to 50, 50 +</td>
<td>Excellent protection</td>
<td>≥ 2.5</td>
</tr>
</tbody>
</table>

Table 1. UPF classification with effective UVR transmission and protection category.

To calculate the UPF value of the fabrics, UV protection measurement of both ZnO NP-treated and non-treated fabrics was performed using a double beam spectrophotometer (Agilent Cary 60 UV-vis spectrophotometer equipped with an integrated sphere to measure both direct and diffuse transmitted light). Each fabric sample was scanned three times by placing at right angle to the incident beam. The spectra were recorded from 290 to 400 nm by means of absorbance and transmission followed by logging the transmittance data for every 5 nm. UPF value was calculated according to the eq. 1. The average UV-B and UV-A transmittance were calculated using the eq. 2 (adopted from [24]) as shown below.

\[
\text{Average UV transmittance} = \frac{T_{\lambda_1} + T_{\lambda_2} + T_{\lambda_3} + T_{\lambda_4} + \ldots + T_{\lambda_n}}{n}
\]

(2)

Where, \(T_{\lambda_i}\) is the transmittance at for every 5 nm (i.e., \(\lambda_1 = 290\) nm, \(\lambda_2 = 295\) nm, \(\lambda_3 = 300\) nm etc.) for a given range of wavelength (UV-B: 290 to 315 nm; UV-A: 315 to 400 nm; UVR: 290 to 400 nm).

ZnO NP-treated fabrics were also investigated by SEM to observe the structure, morphology, and dispersion of the bound-nanoparticles to the fabrics.

**III. RESULTS AND DISCUSSION**

The ZnO NPs required for the treatment of the selected fabrics to improve the UV protection properties were synthesized successfully. It is reported in the literature that the method employed in this study to synthesize ZnO NPs yields nanoparticles with sizes less than 30 nm [8]. The FTIR study was carried out to reveal the purity and nature of the synthesized ZnO NPs. Figure 1 shows the FTIR spectrum of the synthesized ZnO NPs. The broad peak observed at around 3390 cm\(^{-1}\) corresponds to the OH stretching vibration that might be due to the hydroxyl groups of physically adsorbed water molecules. The peaks at 1065 and 450 cm\(^{-1}\) could be assigned to the characteristic absorption peaks of
Zn–O stretching vibration. These findings are similar to the results reported in the literature [25], [26]. Besides, the SEM-EDX survey (Fig. 3b) shows that ZnO NPs are elementally composed of zinc and oxygen, and this revealed that no other elements were detected.

ZnO NPs are considered as UV absorbers since they reflect and absorb UV light. Solar UV radiation can be categorized into UV-A (400–315 nm), UV-B (315–290 nm), and UV-C (290–200 nm). Although sunlight consists all these types of radiation, almost 98% of this radiation, which is UV-A, is passing through the atmosphere and reaching to the earth’s surface. The remaining UV-B (more than 98%) and UV-C are filtered by the ozone layer [27]. In this study, UV protection provided by ZnO NPs was investigated by recording the UV spectra of the nanoparticle-treated fabrics between 400–290 nm. Same procedure was applied for control fabrics as well to avoid other factors which could be of great importance for UPF. By doing so, changes in the UV protection behavior are directly linked to the effect on nanoparticle-treating. UPF-A, UPF-B, and UV transmission values of the tested fabrics were calculated using eq.1 and 2, respectively. The UV transmittance results are shown in Figure 2. All the non-treated fabrics (control ones) showed higher UV transmittance than the ZnO NPs-treated ones between 400 and 290 nm. This indicates that ZnO NPs absorb UV light and reduces UV transmission. Between 315–290 nm, UV transmittance of nylon fabric decreased almost 80%, while that of flax decreased by nearly 20%. A slight decrease in the UV transmittance was observed for polyester fabric (Fig. 2a). Similarly, in the UV-A region shown in Figure 2b, the highest difference in UV transmittance was observed for nylon. This reveals that UV-blocking property of nylon fabric is significantly improved by the ZnO NPs. Additionally, polyester and flax fabrics showed improved UV-protection with respect to the control. Numerical values of % Transmission is provided in Table 2 for clear understanding.
Figure 2. Comparison of calculated UV transmittance values of the ZnO NPs-treated fabrics with the control (non-treated fabrics), between (315–290 nm) (a), and (400–315 nm) (b).

Table 2 shows the calculated UPF factors and % Transmission data of the fabrics which enabled to verify the correlation between % Transmission and UPF. The results revealed that higher UV protection can be attained by treating the fabrics with ZnO NPs, especially for nylon for which UPF increased to 11.02 from 2.12 against UV-B radiation. Although the UPF values for control fabrics (non-treated fabrics) were calculated to be rather low, the obtained data reflect comparable improvements in UV-blocking properties of flax and polyester, and confer very similar UPF values after treating with ZnO NPs. However, the calculated UPFs for the ZnO NPs-treated fabrics were out of the range of the UPF ratings listed in Table 1. Of course, UPF is strongly depended on many factors including fabric composition (made by synthetic and natural fibers or their combinations), construction (woven or knitted which are of significant importance for porosity), thickness, dyeing, color, etc., which influence the overall UPF of fabrics [4]–[7]. Textile fabrics can be manufactured with high UPFs considering the various fabrics’ parameters abovesaid as a separate research study. This study instead focused on the modification of manufactured textile fabrics with ZnO NPs to further increase the UPF to end up with improved UV-blocking behavior.
Table 2. Calculated UPF and % Transmission values of the studied fabrics for UV-B and UV-A radiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UPF</th>
<th>% Transmission</th>
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<tbody>
<tr>
<td></td>
<td>UV-B</td>
<td>UV-A</td>
</tr>
<tr>
<td>Flax (control)</td>
<td>1.69 ± 0.02</td>
<td>1.72 ± 0.10</td>
</tr>
<tr>
<td>Flax (treated with ZnO NPs)</td>
<td>2.84 ± 0.03</td>
<td>2.71 ± 0.22</td>
</tr>
<tr>
<td>Polyester (control)</td>
<td>2.12 ± 0.06</td>
<td>1.87 ± 0.33</td>
</tr>
<tr>
<td>Polyester (treated with ZnO NPs)</td>
<td>2.84 ± 0.08</td>
<td>2.61 ± 0.28</td>
</tr>
<tr>
<td>Nylon (control)</td>
<td>2.12 ± 0.11</td>
<td>1.56 ± 0.25</td>
</tr>
<tr>
<td>Nylon (treated with ZnO NPs)</td>
<td>11.02 ± 1.57</td>
<td>7.40 ± 0.83</td>
</tr>
</tbody>
</table>

The ability of the ZnO NPs to protect the fabric against UVR is directly related to particle content, size and morphology on the treated fabric [20], [21]. Therefore, ZnO NPs-treated fabrics were both visually and morphologically characterized by SEM. Figure 3 shows the micrographs taken from the ZnO NPs-treated fabrics. As can be seen in Figure 3a, ZnO NPs can be clearly defined in the form of large aggregates (shown with blue arrows) of a few tens of micrometers. Some of them are just stacked in the fabric as unbounded flakes (shown with red arrows). Furthermore, not all the fibers were fully covered by the nanoparticles. Besides, the EDX survey (Fig. 3b) confirmed the existence of ZnO in the fabrics. Notably, similar morphology can be seen for ZnO NPs-treated polyester fabric in Figure 3c and d. However, it was noticed that the degree of agglomeration was not as high as observed in treated flax fabric. Besides, nanoparticles were also observed to disperse to some extent along the fibers. In the case of nylon, nanoparticles agglomerate to some extent but they are rather well dispersed throughout the fibers (Fig. 3e and f).
When nanoparticles exhibit dispersion on the fibers, the extent of nanoparticles’ agglomeration was confirmed to reduce. It can be concluded that the largest aggregation was seen in flax and polyester whereas it was the least in the case of nylon. These results imply that morphology of the ZnO NPs was seriously affected by the fabric type. Furthermore, the coarse particles scatter the light causing a slight absorption which means lower UV protection [15]. Therefore, SEM results suggest that UV protection improvement will be the highest for ZnO NPs-treated nylon since particles better dispersed compared to flax and polyester. It can be concluded that our findings from SEM micrographs are in good agreement with the UPF values obtained through UV spectroscopy.

Another reason that may reflect the change in UV protection behavior could be attributed to the nanoparticle content inside the treated fabrics. Interestingly, the nanoparticle contents, which were determined by calculating the difference in weight before and after nanoparticle treatment, are 1.2, 0.9, and 1.5 wt% for flax, polyester and nylon, respectively. The slight increase in the UPF of nanoparticle-treated polyester could be referred also to low nanoparticle loadings onto the flax fabric. It is noteworthy to mention that, although nanoparticle loading onto the flax was comparable to polyester
and nylon, a large amount of agglomeration could not be ascribed only to the nanoparticle loading. This implies that, nanoparticle bounding and agglomeration phenomena can be linked to the fabric’s structure and composition which may possess a selective affinity towards the ZnO NPs. Nylon fabric showed the highest affinity towards ZnO NPs by means of calculated nanoparticle content (1.5 wt%) and it was observed that majority of the particles dispersed at the surface along with only partial agglomeration.

**IV. CONCLUSION**

In this study, influence of nano-zinc oxide nanoparticle treatment on the UV protection properties for the widely used apparel fabrics, which are flax, polyester, and nylon, was investigated by means of UPF calculations. The primary conclusions are as follows: (1) all the tested fabrics treated with ZnO NPs showed improved UV absorption thus increased UPF values are obtained, (2) the highest UPF value was obtained for nylon fabric treated with the nanoparticles. UPF increased by almost sixfold, (3) although the UPF values for the control flax and polyester were around 1.7 and 2, they had nearly the same UPFs after nanoparticle treatment. Compared to nylon, flax and polyester contained large aggregates of ZnO NPs which is presumed to limit the improvement in the UV protection property thus yielding a low UPF, (4) the higher the nanoparticle content does not signify the formation of agglomeration as a sole effect. Besides, the affinity of the fabrics towards nanoparticles is also another issue that must be considered. Although, nylon fabric had the highest nanoparticle content among the others, interestingly, SEM micrographs displayed reduced agglomeration and increased dispersion behavior which is ascribed to higher affinity of nylon towards ZnO NPs when compared to flax and polyester.

**V. REFERENCES**


