Concept Evaluation of Predicting UPF Values for Artificial Cellulose Fabrics by Varying the Optical Brightener Chemical Structure Applied

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Abstract

The publication presents investigation results and statistical analysis showing that by varying the chemical structure of optical brighteners from the derivative group of stilbene used for fabrics of artificial cellulose fibre modification, resulting in a different manufacturing process, it is possible to predict the level of the UPF value of the index of such modified fabric. In addition, statistically it was confirmed by results from early research that both the fibre finish (in this case, roughening the pigment TiO₂) used for fabric manufacture as well as the FBA concentration used for fabric modification influence their UPF index value. Fabric UV-barrier studies also showed that despite a partial decrease in UPF values for such finished fabrics, the dependence of such an index on subtle differences in the chemical structure of the FBAs is maintained. Primarily the possibility and range of improving textile barriers against UV radiation through the use of the UV-absorption abilities of optical brighteners with subtle differences in their chemical structure was recognised, creating a premise to elaborate a mathematical control concept to steer a textile UV-barrier.

Key words: artificial cellulose fibres, fabrics, fluorescent brightening agents FBAs, ultraviolet protection factor UPF, spectrophotometric analysis, one-way ANOVA statistical analysis.

Introduction

Health as an area covering, among others, the problem of an ageing society, cancer fatalities, materials as well as health hazards determined by the environment, is one of the strategic research areas and the priority research direction of the Polish National Framework Programme (KPR) [1], along with the Polish National Development Strategy 2007-2015 [2]. The concern of excessive exposure to UV radiation effects is focused on the dangerous health problem mainly caused by the ultraviolet wavelength range region of the UVB, which excessively affects the DNA structure and can lead to mutations and the formation of cancerous conditions that weakens resistance to viral diseases and parasitic infection, not to mention that it is hazardous for the eyes as well [3-8]. The opinions in recent years about the action mechanisms of UV radiation on skin testify the contribution of UV A radiation in the process of skin aging, carcinogenesis, immunosuppression, and induction photo dermatoses [9, 10]. The increase in awareness of the hazards of excessive sun exposure and the impact of UV radiation on the human body has increased research on barrier solutions to UV radiation. Cosmetics containing a UV absorber have become recommended skin protection against the adverse effects of UV radiation, especially when used alongside clothing designed to provide a barrier to UVB and UVA radiation [11, 12]. All textiles from which protective clothing against the adverse effects of UV radiation are manufactured must comply with the barrier condition, which specifies a respective rate of UPF [13]. The test results presented in scientific literature are focussed primarily on the physical barrier aspects of fabric, knitted fabric or yarn from which textiles are produced [14-16]. Gradually the impact of chemical agents has been analysed and highlighted, i.e. the type of (construction) dye to improve the barrier properties of products with regard to UV radiation [17] and the beneficial effects of different types of absorbers applied in the process of product finishing [18-21], which increase the protective properties thanks to their strong ability to absorb radiation in the UV range. The task of FBAs commonly used in finishing textile products is to absorb radiation in the near ultraviolet range and emitting radiation in the blue range of the visible spectrum and to correct the colour visual effect, especially for white articles.

Our findings when using our own UV-spectrophotometry showed that optical brighteners can be a multi-purpose additive for improving not only the product’s visual effect, but it may also increase the barrier properties of textiles with respect to UV radiation, as well as
protrect the fibre material from undergoing destruction [22, 23]. Regarding the barrier properties of the test fabric model with different types of fibres, some effect was presented by the type of fibre polymer, the presence of a matting agent and the parameters of the fabric structure, but not large enough to significantly improve the UPF value. The main improvement is observed for most fabrics obtained by the introduction of fibre optical brightener molecules. The UPF factor value achieved for optically brightened fabric exceeded the threshold value that corresponds to fabrics with very good protective properties [24].

In this publication, the authors quote trial results and analysis looking for the possibility to control the UPF index of fabrics made out of cellulose fibres through the use of optical brightener FBA’s UV-absorption abilities.

**Experimental details – materials and method of investigations**

The experimental materials used were raw modal plain weave fabric manufactured by Lenzing AD Austria with bright and dull artificial cellulose fibres: standard viscose (CV), modal type (CMD), and lyocell type (CLY), whose characteristics are presented in Table 1. Intentionally more detailed information about the structure of these fibers is not provided, as the authors are preparing a separate publication which analyses the relationship between the fibers structure and barrier against UV radiation.

In order to improve the textiles’ UV radiation absorbance characteristics, modal fibre samples were subjected to the optical brightening modification process according to Industry Standard BN [25]. Appropriate and widely used optical brighteners were applied constituting those of a 4,4’-Diaminostilbene-2,2’-disulphonic acid derivative, whose schematic structure can be observed in Figure 1. Characterised with fairly good durability to light (Xenotest: A – 3, B – 3/4, C – 3 according to the grey scale). Depending on the functional group types X and Y, various kinds of brightening agents can be produced out of this chemical group. The formulas of functional groups used in the study are shown in Table 1.

The optical brightening process was carried out with the water bath method. An AHIBA laboratory pressure dryer was used for this purpose, in which there was a constant bath volume at constant temperature as well as intense sample mixing. Fabric samples were brightened in accordance with the general terms and conditions recommended by the manufacturer: bath module: 1:20-1:40, bath concentration of the brightener during the bath: i.e. 0.05 and 0.3S%. The sample exposure process was carried out using Xenotest apparatus (Atlas, Germany) continuously for a time period of about 100 hrs – until a contrast equal to 4 on the grey scale appeared, resulting in the most robust sample. In this case blue wool patterns identified by numeric indicators from 1 to 8, developed and made in Europe, were used, characterised by diverse light resistance from 1 – very low to 8 – very high. The exposure was performed under climate conditions: air humidity: Φ = 40-60%, BST: T = 50°C and chamber temperature: T = 30°C. The UPF index was assigned in vitro in an Integrated Ulbricht Sphere (Germany) using the UV spectrophotometric method for measuring UV penetration through the fabric of clothing, based on the assumptions of European Standards EN [13], by placing the test object in between the radiation beam of the illuminant and integrating sphere, thanks to which it is possible to take into account the measurement of the total radiation emerging from the sample, i.e. directional and diffuse radiation. The measurement was carried out under normal conditions of relative humidity: Φ = 33% and temperature: T = 21°C. In order to measure the total passing coefficient of the optically brightened fab-

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**Figure 1. Schematic molecule structure of optical brighteners constituting the trans 4,4’-Diaminostilbene-2,2’-disulphonic acid derivatives and functional groups X and Y formulas applied, which differentiate the FBA types: A, B and C.**

**Table 1. Characteristics of artificial cellulose fibres and fabrics made from these fibres.**

<table>
<thead>
<tr>
<th>Characteristics of textiles</th>
<th>Fabric symbol</th>
<th>No. of yarn in both directions</th>
<th>Density of weave (warp/weft)</th>
<th>Thickness of fabric, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric of artificial cellulose viscose fibres, bright plain weave</td>
<td>F-CV-b</td>
<td>1.3 dtex/39</td>
<td>320/270/10 cm</td>
<td>0.23</td>
</tr>
<tr>
<td>Fabric of artificial cellulose viscose fibres, dull plain weave</td>
<td>F-CV-m</td>
<td>1.3 dtex/39</td>
<td>320/270/10 cm</td>
<td>0.25</td>
</tr>
<tr>
<td>Fabric of artificial cellulose modal fibres, bright plain weave</td>
<td>F-CMD-b</td>
<td>1.3 dtex/39</td>
<td>320/270/10 cm</td>
<td>0.22</td>
</tr>
<tr>
<td>Fabric of artificial cellulose modal fibres, dull plain weave</td>
<td>F-CMD-m</td>
<td>1.3 dtex/39</td>
<td>320/270/10 cm</td>
<td>0.25</td>
</tr>
<tr>
<td>Fabric of artificial cellulose fibres of lyocell type, bright plain weave</td>
<td>F-CLY-b</td>
<td>1.3 dtex/38</td>
<td>320/270/10 cm</td>
<td>0.22</td>
</tr>
</tbody>
</table>
rics, a non-fluorescence filter was used that does not allow to pass radiation in the visible range i.e. $\lambda = 400-700$ nm but transmits UV radiation in the range of $\lambda < 400$ nm [26]. The barrier effect of the model fabrics was rated by determining the ultraviolet protection factor (UPF) [13], in other words the numerical value indicating the UV radiation protection level (see Equation 1) [13], taking into account the sensitivity of human skin to UV radiation. Such a calculated result indicates how much longer skin covered with such an article may be exposed to solar radiation as compared to bare skin.

$$\text{UPF}_i = \frac{\sum_{\lambda=300}^{\lambda=360} E(\lambda) \varepsilon(\lambda) \Delta \lambda}{\sum_{\lambda=300}^{\lambda=360} \varepsilon(\lambda) T(\lambda) \Delta \lambda}$$

(1)

where:
- $E(\lambda)$ – solar light spectrum measured in Albuquerque, often used by dermatologists in Europe (W/m² nm⁻¹)
- $\varepsilon(\lambda)$ – relative erythema effectiveness
- $T(\lambda)$ – spectral transmittance at wavelength $\lambda$ (permeability of protective object – textile product)
- $\Delta \lambda$ – wavelength interval of measurements (nm)

For all fabrics the spectral transmittance coefficients values were measured in the 300-360 nm wavelength range, considering the range $\lambda = 305-315$ nm, which has the greatest importance in barrier analysis. The European Standard [27] assumes a threshold for clothing that meets protective properties against UV radiation at a level of “UPF 40”; in this paper, however, Australian and New Zealand’s classification standards were used [28], according to which textiles are classified as UV protection cases where they have a UPF index at a level of >15 – see Table 2. According to recent testing [29], a UPF value around 30 is typical for protective fabrics, while that around 6 is typical for standard summer fabrics.

The durability of the barrier effect achieved was analysed based on the UPF index obtained for fabrics tested after UV radiation exposure.

### Results and discussion

One-way ANOVA analysis of variance was carried out with the help of Minitab® 17 Statistical Software for the UPF index value obtained for diversified manufacturing process fabrics of artificial cellulose fibres both bright and dull, optically brightened with three types of FBAs (A, B and C) with minimal and maximal concentration and assuming a significance level of 0.05. The software used pooled standard deviation to calculate the intervals.

In order to carry out statistical analysis of the barrier test results before being exposed to UV radiation as well as to assess the durability of the barrier effect achieved, it was necessary to index all UPF values determined by the UV specktrhemetric method according to the scheme presented in Table 3, identifying them as UPF-i. The before and after UV radiation exposure index results are presented in Table 4.

For statistical analysis of fabrics made of bright and dull artificial cellulose fibres treated with maximum and minimum concentration of optical brightener both before and after UV radiation exposure, the following assumptions were assumed: the null hypothesis $H_0$ states that all means do not differ from each other.

### Table 2. Classification of standard values for UPF factor of fabrics and clothing, along with the percentage values of UV protection. Note: Own source, based on the standard [28].

<table>
<thead>
<tr>
<th>UPF protection category</th>
<th>UPF range</th>
<th>UPF rating</th>
<th>UV protection value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good protection</td>
<td>15 to 24</td>
<td>15, 20</td>
<td>93.3-95.9</td>
</tr>
<tr>
<td>Very good protection</td>
<td>25 to 39</td>
<td>25, 30, 35</td>
<td>96.0-97.4</td>
</tr>
<tr>
<td>Excellent protection</td>
<td>40 to 50, 50+</td>
<td>40, 45, 50</td>
<td>97.5-98.0+</td>
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</tbody>
</table>

### Table 4. UPF and UPF-i values for fabrics made of bright and dull artificial cellulose fibres treated with maximum and minimum concentration of optical brightener – before/after UV radiation exposure together with zero variant – without FBA. Note: Own source, based on studies.

<table>
<thead>
<tr>
<th>UPF &amp; UPF-i</th>
<th>Values of UPF and UPF-i (before/after exposure to UV radiation)</th>
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<tbody>
<tr>
<td>Fabric symbol</td>
<td>without FBA</td>
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<tr>
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<td>---------------</td>
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<tr>
<td></td>
<td>before</td>
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<tr>
<td>F-CV-b</td>
<td>4</td>
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<td>F-CV-b</td>
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<tr>
<td>F-CV-m</td>
<td>29</td>
</tr>
<tr>
<td>F-CV-m</td>
<td>25</td>
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<tr>
<td>F-CVM</td>
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<td>F-CMD-m</td>
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are equal, and the alternative hypothesis $H_1$ states that not all means are equal for a 95% confidence level $\alpha = 0.05$.

According to the results shown in Table 4, fabrics with artificial cellulose fibres gain a better UPF (UPF-i) after applying FBAs from the derivative group of stilbene. Particularly high values of UPF (UPF-i) where achieved for fabrics which were previously roughened with TiO$_2$ pigment of diffusing incident light properties. The resulting value remains similar after exposure to UV radiation. In order to verify the significance level among the test results obtained, a one-way ANOVA analysis of variance was carried out. As a result, the test presents a p-value of 0.000, which is less than the significance level $\alpha$ and allows to reject the null hypothesis $H_0$. Hence the type of fibre surface finishing (fibre roughing) has a significant influence on the fabrics UV-barrier; additionally, it is preserved after the sample’s exposure to UV radiation, whose results also presents a p-value equal to zero. The relation between UPF and FBA concentration applied to the fabrics was also found with the aim of confirming data from earlier foreign publications [14], which affirm that the concentration of the dyeing auxiliaries (in this case the brightener) has a barrier effect on textile products against UV radiation.

Statistical analysis of the use of maximum and minimum brightener concentration on all fabrics tested shows a p-value of 0.008, which is less than the significance level $\alpha$ and allows to reject the null hypothesis $H_0$. There is a significant difference between the means of the minimum and maximum c. Taking into account all data, it can be concluded that for the maximum brightener C a higher UPF value is obtained. This relation is also maintained after exposure to UV radiation, for which p-value = 0.010 i.e. a significant difference between the maximum and minimum c means can be observed.

The main purpose of the experiment was to analyse the relation between the UPF value and FBAs (different functional groups X and Y) used to modify the fabrics. For this case, statistical analysis of all samples presented a p-value of 0.437, which is bigger than the significance level $\alpha$ and does not give any basis to reject the null hypothesis $H_0$. Hence, even though in the case of using brightener A there is an apparent difference in the UPF (UPF-i) value in relation to the other two brighteners. After exposure to UV radiation the UV-barrier values are almost at the same level. The p-value of 0.752 does not confirm significant differences between all brighteners mean used, and therefore the null hypothesis $H_0$ where all means are equal, cannot be rejected.

Separating the results for the minimum and maximum concentration of the FBAs, it can be observed that in case of the first ones the p-value = 0.997, which is bigger than $\alpha$, does not allow to reject the null hypothesis $H_0$. This fact excludes the possibility to observe significant differences between the means of UPF values resulting from the use of different functional groups on the FBA chemical structure. The exposure to UV radiation of fabrics modified with the minimal concentration c of FBAs did not cause significant changes in the results, giving a p-value of 0.941.

The situation looks different when using the maximal concentration of FBAs, where analysis presented a p-value of 0.016 (Figure 2), which shows that there is a significant difference between means, allowing to reject the null hypothesis $H_0$. The Tukey comparison was used to determine which means are significantly different, with results showing that there is a significant difference between the means of brighteners A and B as well as brighteners A and C. The results show that by modifying the fabrics with a bigger concentration of brighteners A and C, they present a higher UPF index than in the case of modifying the fabrics with the maximum concentration of brightener A. On the other hand statistical analysis of the durability to the UV radiation test (Figure 3) presents that the results change, with a p-value = 0.221, which is bigger than the significance level $\alpha$, therefore it is not possible to reject the null hypothesis $H_0$ as there are no significant differences between the means.

Further analysis was carried out separately for bright and dull fabrics whose aim was to acquire more accurate data on the impact of the application of the various functional groups on the FBA chemical structure upon the UPF. The results obtained for dull fabrics brightened with...
maximum c excluded the possibility of any further analysis due to the fact that the indexed values UPF-i were formed at a similar high level (50) both before and after exposure of the fabrics to UV radiation.

One way – ANOVA was carried out for bright fabrics brightened with the maximum concentration of FBAs. The p-value of 0.000 (Figure 4) shows that there is a significant difference between the means and there is enough proof to reject the null hypothesis $H_0$. Moreover the Tukey pairwise comparison indicates that brighter A used (which presents a good UPF level) had a different mean from those of fabrics in which brightener B was used as well as from those in which brightener C was used (both cases presented an excellent level of UPF). After exposing the fabrics to UV radiation, the results of UPF decreased for all samples; however, with a resulting p-value of 0.045 (Figure 5) they preserve the significant difference in the means of fabrics using brightener A and other fabrics using brighteners B and C means.

### Conclusions

The aim of the examinations and analysis was to show that the UPF value may be dependent upon differences in the chemical structure of an optical brightener from the derivative group of stilbene used for fabrics of artificial cellulose fibre modification, resulting in a different manufacturing process. However, a thorough analysis is needed for further carefully designed studies.

The one way-ANOVA analysis showed that the main objective of the studies undertaken was achieved: to confirm the existence of a statistically significant relationship between the values of UPF obtained and subtle changes resulting from variations in functional groups X and Y of the FBA chemical structure (type A, B and C) used to modify the artificial cellulose fibre fabrics. The impact of differences in the chemical structures of the stilbene derivative compound on the UPF index can be mainly observed from variations in functional groups X and Y of the FBA chemical structure. The impact of differences in the chemical structures of the stilbene derivative compound on the UPF index can be mainly observed from variations in functional groups X and Y of the FBA chemical structure. The impact of differences in the chemical structures of the stilbene derivative compound on the UPF index can be mainly observed from variations in functional groups X and Y of the FBA chemical structure. The impact of differences in the chemical structures of the stilbene derivative compound on the UPF index can be mainly observed from variations in functional groups X and Y of the FBA chemical structure.

Analysis of the possibilities and textile barrier against the UV radiation improvement range by utilising the UV-absorption capacity of optical brighteners with subtle differences in their chemical structure creates a premise to elaborate a mathematical control concept to steer the textile UV-barrier. However, an extension of the research is required based on precise numbers and a larger sample as well as the application of FBAs with optimal durability to UV radiation that will allow for comprehensive diagnosis of complex processes taking place inside and outside the fibre during its modification, depending on the brightener chemical structure changes.

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