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Reduction of radiation transmission through functionalization of textiles from man-made cellulosic fibers

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ABSTRACT

Both ultraviolet (UV) and infrared (IR) light have negative impact on the human health. With this background it is the main aim of the current research to realize a textile material which is able to protect against both UV light and IR light. For this research, regenerated cellulosic fibers from the Lyocell process are used and modified. Main analytical investigations are done by photo-spectroscopy in arrangement of diffuse transmission for the spectral range from 220 nm to 1400 nm. Additionally, microscopic investigations are done by scanning electron microscopy (SEM). For material development, Lyocell fibers functionalized with TiO_2 particles are first processed into yarns and then into knitted fabrics. Compared to non-functionalized textiles, the transmission is reduced in the UV range due to the absorption behavior of TiO_2. Subsequent dyeing with anthraquinone or reactive dyes enhanced the UV protective effect. To reduce the transmission in the near IR range (NIR), non-functionalized Lyocell knitted fabrics are functionalized with various IR absorbers in different concentrations. With increasing concentration, the transmission decreased. However, a grey coloration of the textile is observed simultaneously, with increased concentration. This must be considered in further processing steps. With these methods for functionalization, it is possible to produce textiles that offer increased protection against UV and IR radiation. These are promising materials for the production of clothing or work wear.

Keywords
Lyocell,
UV-protection,
IR-protection,
radiation protection,
skin care,
TiO_2,
anthraquinone dye,
perylene dye,
functionalization

1 Introduction

The skin is the largest human organ. It is permanently affected by environmental influences and reacts to them. Exposure of chemicals or radiation can lead to skin damage or even skin cancer [1]. The negative impact of ultraviolet light (UV light) on the skin is well known. This radiation leads to sun burns, accelerated skin ageing and skin cancer [1-4]. In contrast, the negative impact of infrared light (IR light) on the human skin is less known but such effects on the human skin are discussed recently [4-6]. Also, beneficial aspects of IR radiation on the skin are discussed [7]. Likely pathways involve the modulation of intracellular levels of reactive oxygen species by the production of melatonin which is known for protective effects in the skin. However, beneficial effects seem to be strongly dependent on the applied amount, so an attenuation of the IRA irradiance can be reasonable [8]. There are actually even cosmetic products on the market proposing a protection against both UV light and IR light [9-11]. However, these cosmetic products do not cover textile developments. Beside sun protective cosmetics, especially textile materials play an important role in skin protection. Nevertheless, often conventional textiles offer only limited protection against aggressive radiation, such as UV or IR irradiation [12,13].

The protective effect of textiles can be increased by functionalization, protective finishing and textile construction [12,14-18]. Especially the application of UV-absorbers should be mentioned [19-21]. Organic UV-absorbers are mostly uncolored compounds with a strong capability to absorb UV-light and excellent light stability [22-25]. Inorganic UV-absorbers consist of pigments from semiconductors, such as TiO_2, ZnO or CeO_2 [26-29]. The effectivity of inorganic UV-absorbers is often also described by their band gap energy, which determines the maximum wavelength of light which can be mostly absorbed [23,30,31]. For this, these inorganic absorbers exhibit an absorption edge. Also, dyeing processes and antimicrobial zinc complex compounds can enhance the UV protective properties of textile fabrics [32-38]. Textiles coated with special effect pigments or microscopic basalt staple fiber can additionally contribute to an UV-protection and a certain decrease of IR light transmissibility [39-42]. The simultaneous release of skin care products (e.g. vitamins) from a functionalized textile to the skin can support skin regeneration. By this, the regeneration of skin damages caused by radiation is possible. Recently the combination of radiation protection with skin care products on textile materials is defined as a “biophysical skin care concept” [43]. In the presented work, bi-functional textiles based on cellulosic Lyocell fibers with a protective effect against damaging radiation and a skin care component are aimed. In earlier investigations, X-ray absorption was developed and related fabrics were produced from it. To realize such a special functionality as X-ray protection, inorganic X-ray absorbers such as barium sulphate ($BaSO_4$) or bismuth oxide (Bi_2O_3) are embedded in Lyocell fibers in high concentrations [44-46]. In contrast to these earlier studies, the recent investigations are aiming at the possibilities of UV and IR protection, which are strongly related to applications in the area of sport textiles, outdoor clothes and wellness textiles.

For this purpose, different methods for reducing the transmission of irradiation are investigated: a) addition of TiO_2 particles into the spinning mass of the cellulose fibers, b) dyeing of textiles with relevant dyes, and c) functionalization of textiles with organic and inorganic absorbers. A comparison of these three approaches is one aim of the current investigation. The different resulting textiles are compared regarding their effectivity in radiation protection by investigation with photospectroscopy performed for the spectral range from 220 nm to 1400 nm.

2 Experimental section

2.1 Materials

Lyocell staple fibers with 2% titanium dioxide (TiO_2) as absorber component and Lyocell staple fibers without functional additives as reference fibers are used. The staple fibers are produced as B-type (1.7 dtex, 38 mm). The dispersion technique for the addition of inorganic powder is developed experimentally and optimized with regard to achieve a stable dispersion and the associated good distribution of the solid particles in the cellulose matrix. Dispersing the titanium oxide powder in a partial amount of the solvent used (60 % N-methylmorpholine N-oxide / NMMO) is done by means of an Ultraturrax at 10 min treatment time. As Ultraturrax equipment a device Ultra-Turrax T 50 (IKA-Werke GmbH & CO. KG, Staufen, Germany) is used. The dispersion time is set to 10 min and the dispersion speed is 5,000 rpm.

Different commercially available dyestuffs are used for application on the Lyocell fiber materials. These are vat dyes with a proposed NIR protective effect were supplied by DyStar (Indanthren Yellow 5GF Colloisol – Yellow shade – and Indanthren Yellow 3R Colloisol – Orange shade). Additionally, a conventional reactive dye as well supplied by DyStar is applied – Levafix brilliant Yellow CA gran. For IR absorbency, experimental products supplied by the company Textilchemie Dr. Petry GmbH (Reutlingen, Germany) are evaluated. These IR absorbers are distinguished into one organic absorber (QD300+) and two hybrid absorbers (QD300i, QD300q). The hybrid absorbers are a combination of the organic absorber QD300+ with the inorganic component lanthanum hexaboride (for QD300i) or a cesium tungsten oxide (for QD300q).

2.2 Procedures and preparations

The Lyocell fibers mentioned above were spun alone. All yarns were created on a rotor spinning machine from Schlafhorst (Schlafhorst Oerlikon Autocoro 480 e-save) in yarn counts Nm 30 to Nm 40. For the knitting process, the yarns have been spun and paraffinized with a twist of approx. 680-790 T/m. In order to test the different dyes and finishes, single jersey tubular fabrics were created on a circular knitting machine (Harry Lucas TK-83-L) gauge E24, which were subjected to a prewash (60 °C, 60 min) before finishing.

As dyeing machine for application of the vat dyes and the reactive dye, a Polycolor supplied by Zeltex AG is used. The liquor ratio for dyeing in this machine is set to 1:10. For the vat dyes the process temperature is set to 50°C with a duration of 60 min. The application of the reactive dye is done at 60 °C for 60 min. The recipe for applying the vat dyes contain following components vat dye (3%); Meropan DPE (2 g/L); Kollasol CDS (0.5 g/L); Sarabid VAT (1%); $NaOH_{aq}$ (1.5%), sodium hydrogensulfite (3.87 g/L), Na_2SO_4 (10 g/L) and soft water as solvent. The rinsed fabrics are then passed through oxidation with Sera Con M-LV (supplied by DyStar) in a concentration of 3 g/L (20 min at 60 °C). Finally, the samples are cleaned in a Mathis SOAPY by soaping with CotoBlanc RS in a concentration of 1 g/L (20 min at 100 °C). After 60 seconds of spinning, drying at room temperature is performed. The recipe for applying the reactive dye contains the following components: reactive dye (3%), Na_2SO_4 (50 g/L); NaOH (1.85 g/L); Sarabid MIP and soft water as solvent. After dyeing, the samples are rinsed and washed in a Mathis SOAPY at 60 °C (10 min), 95 °C (10 min) and 60 °C (10 min). Afterwards, a rinsing with citric acid (20%) is done at room temperature. Finally drying at room temperature is performed. For the finishing of textiles with IR absorbers, three samples per concentration are prepared in a size of 6 cm x 6 cm. These textile samples are loosely folded, placed in a snap lid glass with 20 g solution and wetted for 15 sec. Afterwards the padding is performed twice and the samples are placed on paper. For this, a padding device supplied from Ernst Benz is used. The wet uptake was approximately 100%. Between the respective concentrations, the padding machine is cleaned with water. All samples are placed in the drying cabinet (Memmert) for 60 min at 40 °C.

2.3 Analytical methods

The diffusive transmission of the realized textile fabrics is measured in the spectral range from 220 nm to 1400 nm. By this measurement, the protective effect against UV-light in the range of 220 nm to 400 nm can be determined. The protective effect against IR light is determined for the range of 700 nm to 1400 nm. These spectroscopic measurements are performed with a photospectrometer type UV2600 supplied by Shimadzu (Japan). This spectrometer is equipped with an integrating sphere enabling the measurement of diffusive transmission. Microscopic investigations are done using a scanning electron microscope (SEM) Tabletop TM3000 supplied by Hitachi (Japan).

3 Results and Discussion

3.1 Functionalized fibers by additives in the spin mass

To gain radiation protective properties, radiation absorbing components can be embedded into the fiber during the fiber production process. Actually, the use of the inorganic UV-absorber TiO_2 is investigated, which is added as particles to the spinning mass for Lyocell fiber production. TiO_2 is an excellent white pigment but also a widely used UV-absorber [12,22,47,48]. Figure 1 shows a microscopic image of the investigated TiO_2 containing Lyocell fibers. Several embedded TiO_2 pigment particles are visible on the cellulosic fibers as white spots. Areas containing materials of higher atomic weight, such as titanium compared to carbon or oxygen, appear on SEM images brighter. For this, SEM does not only support topographic information on the samples, but also a certain material contrast is visible [49]. In Figure 1 the regular distribution of the embedded TiO_2 particles is clearly visible.

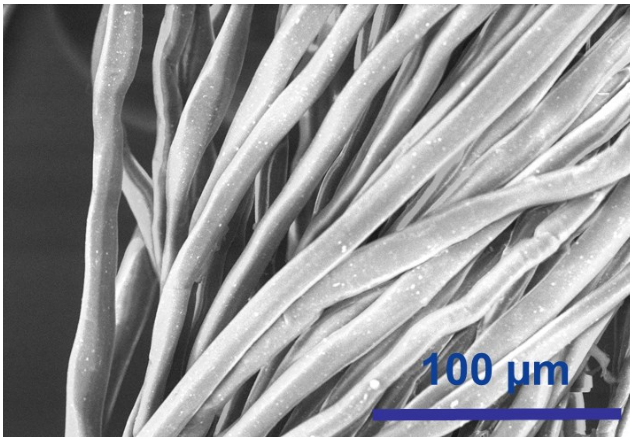

Fig. 1 SEM image of Lyocell fibers containing titanium dioxide TiO_2 particles.

Lyocell fibers with embedded TiO_2 particles are used for the production of knitted fabrics. Their diffusive transmission is determined and compared to the transmission of an analogous Lyocell fabric without any further UV absorbing additive (Figure 2). The recorded transmission spectra of both fabrics exhibit a significant difference in the spectral range of <400 nm (for UV-light). Due to the band gap energy of the UV-absorber TiO_2, a strong decrease in transmission for light with a wavelength lower than 380 nm can be determined [23]. It is clear that UV-protective properties can be introduced to Lyocell fibers by embedding TiO_2. However, for the visible and near-infrared spectral range the shape of the transmission spectra is nearly similar, no matter if the Lyocell fibers contain TiO_2 or not. The addition of TiO_2 leads to clear UV-protective properties but a protection against infrared light cannot be reached.

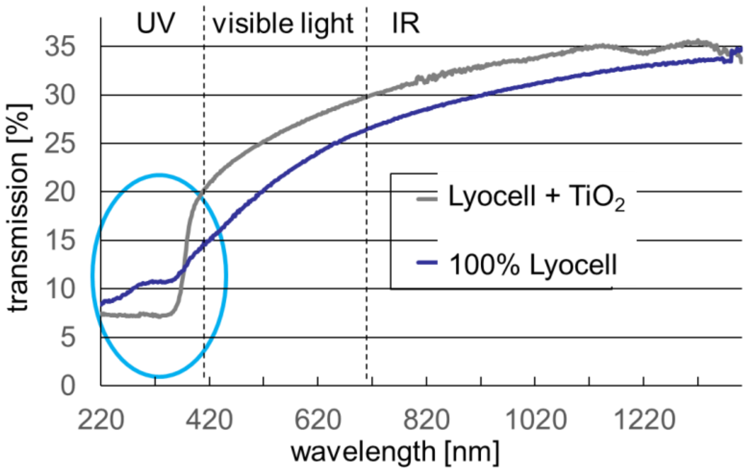

Fig. 2 Spectra of diffusive transmission – comparison of a Lyocell fabric and a fabric from TiO_2 containing Lyocell fibers. The UV area is especially indicated.

3.2 Dyeing of textiles

It is often reported that coloured fabrics exhibit better UV protective properties compared to similarly produced white fabrics [12]. This effect is favoured by the fact that many dyestuffs do not only interact with visible light but also absorb UV-light [32,33,51]. Such an effect is also reported for coatings containing effect pigments [41]. Further, it is known that dyestuffs can also be used for infrared camouflage applications [52-54]. The aim in such cases is to realize a material having similar spectral reflective properties as green leaves to accommodate a camouflage effect. Therefore, such dyes absorb in the red and blue section of the spectrum and transmit green as well as near infrared approx. between 800 nm and 1200 nm (NIR) [55]. The textile material dyed with such molecules or pigments will then reflect the remaining green and NIR parts of the spectrum, which reproduces more or less effectively the remission of green leaves. However, for NIR protection purposes such dyestuffs render inadequate since high absorbency in this respective spectral region is needed. This aim is challenging since most organic dye molecules exhibit strong absorbencies in the visible as well as in the far infrared spectral range. The former is caused by electronic transitions, energy differences between suitable molecular orbitals. This involves usually the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Far infrared absorptions are caused by transitions of suitable vibrational states in a molecule, so an absorption of a photon leads to an increase of the vibrational frequency of a molecule or a molecular subgroup [56]. Furthermore, the effectiveness of either absorption is dependent on the transition dipole moment, which differs for molecules and substructures.

The energy range of either type of transition is limited and so is the spectral range in which it can occur. The energy difference, and therefore the potentially absorbed wavelength, between HOMO and LUMO is roughly inversely correlated with the spatial extension of such orbitals across the molecular structure [57]. Ways to obtain large orbitals and therefore acquiring some absorbency in the NIR range can be achieved by the introduction of conjugated pi-systems. However, such systems will additionally absorb UV light, too, which leads to short lifetimes of such molecules under light exposure in general.

On the other hand, the energy difference of vibrational states depends on the mass of the involved atoms and the strength of the connecting chemical bond and can therefore not be increased sufficiently to shift absorbencies in the NIR range. For this, most molecules exhibit a gap in the spectral absorbance between the visible and the NIR range. IR-A absorbing organic dyes therefore have to rely on extended pi-systems. Anthraquinone dyes offer such systems and may be an option to realize IR-A absorbing effects in textiles at least to some extent.

In the recent investigation, three different dyes are considered for the treatment of Lyocell fibers. These dyes are two vat dyes of anthraquinone type and one reactive dye. To illustrate the colour impression of dyed Lyocell fabrics, related photographs are presented in Figures 3 and 4. Before application of the dyestuffs, the fabrics appear white. In presence of the TiO_2 the whiteness is improved due to the reflectance of this white pigment. The yellow and orange coloration of dyed Lyocell fabrics is obvious (Figure 4). It has to be stated that a yellow coloration of a material is often related to its potential to act as UV-protective material [22, 58]. This feature is most probably related to a broad absorption band in the region reaching into the visible range of the spectrum.

Fig. 3 Color impressions from Lyocell fabrics with and without TiO_2 additive before application of the dyestuffs.

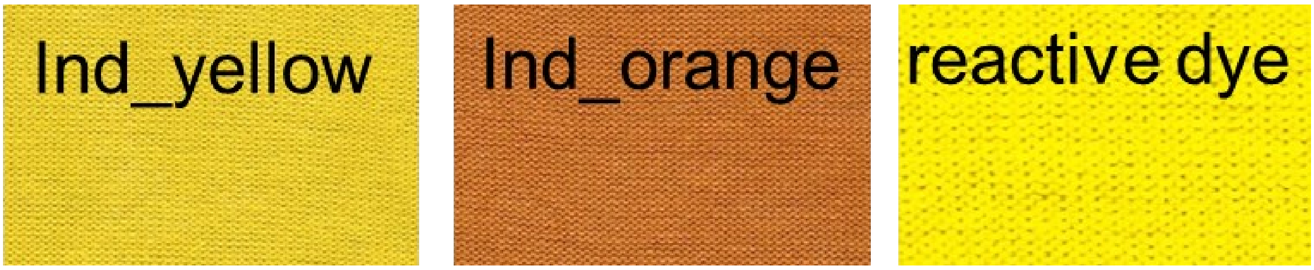

Fig. 4 Color impressions from Lyocell fabrics dyed with the different dyestuffs.

The concept of combining of inorganic UV-absorbers like TiO_2 and organic UV-absorbers to reach an optimal UV-protection is well known for coatings on glass substrates and polymer foils [22,59,60]. Also, for textile substrates such a combination is reported. Many relevant reports in this area are related to the use of nanoscaled TiO_2 particles and organic UV-absorbers combined in a coating application [61-63].

In the current investigations, the IR-protection is additionally elicited by the dye application on a TiO_2 containing Lyocell fabric. The improvement of transmission reduction by this approach is presented in Figure 5 for the spectral range from 220 nm to 1400 nm. In this figure, the reduction of transmission after dyeing of the fabrics in comparison to the undyed TiO_2 containing Lyocell fabric is recorded as a spectrum. With all three investigated dyestuffs, the transmission for UV light is further decreased. This improvement is especially shown in the spectral region from 380 nm to 400 nm, where the absorption of TiO_2 is lower, so the applied dye can improve the UV absorption drastically. The UV protection caused by the embedded TiO_2 can be further improved by dye application.

However, by view on the spectral range of near-infrared light, the reduction of transmission is lower and in maximum only values around 30% are reached. These effects in the IR-region are only achieved by dyeing with Indanthren Orange, while the other two investigated yellow dyes are less effective. It can be concluded that the dye application improves the performance due to UV-protection significantly, while the influence on a proposed IR protection is only low to moderate. Additionally to the improved radiation protective properties, a coloration of the treated fabrics appears, which may not be suitable for every type of clothing application.

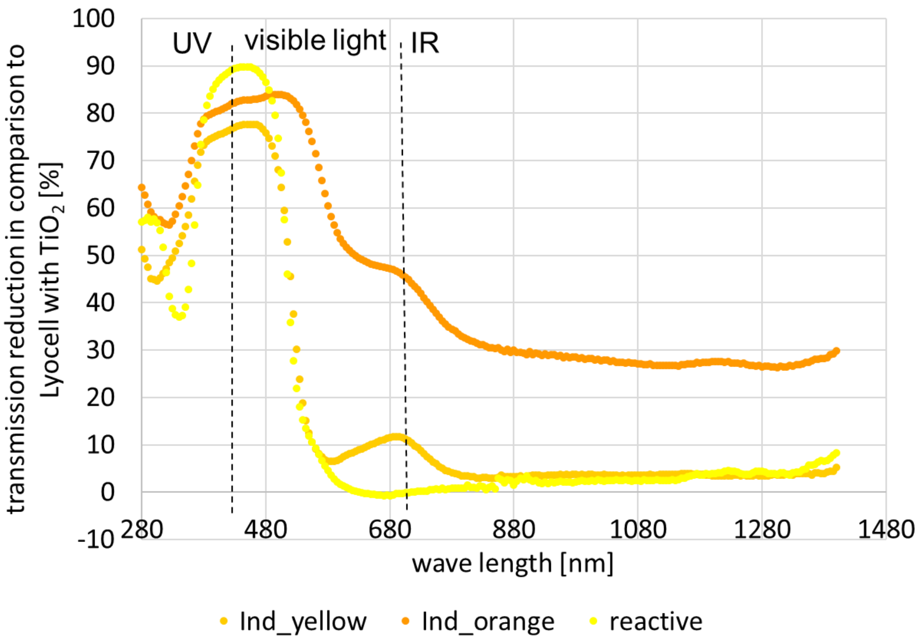

Fig. 5 Comparison of transmission reduction after dyeing of a TiO_2 containing Lyocell fabric with different types of dyestuffs.

3.3 Application of infrared absorbers

Infrared absorbers (IR-absorbers) are dedicated to absorb especially infrared light, while mainly no visible light is absorbed. This is the main difference to the dyes presented in the former sub-section. Nevertheless, if the IR-absorbers are applied in higher concentration, they also change the coloration of the treated Lyocell fabric (Figures 6 and 8). In these Figures 6 and 8 the reduction of transmission after application of the IR absorber on the fabrics in comparison to the untreated Lyocell fabric is recorded as spectra. For treatment of Lyocell fibers, two types of IR-absorbers are evaluated – so-called organic absorbers (most effective in the spectral range of 600 nm to 800 nm) and so-called hybrid absorbers (effective in a wider spectral range of 600 nm to 1400 nm).

The reduction of transmission after application of the organic absorbers is presented in Figure 7. It is clearly seen that this type of absorber is effective up to a wavelength of 900 nm. However, IR light of higher wavelength is mainly not influenced by this absorber. Also, it is clear by view on the spectra that this IR absorber has a significant influence on visible light and therefore on the coloration of the treated fabric.

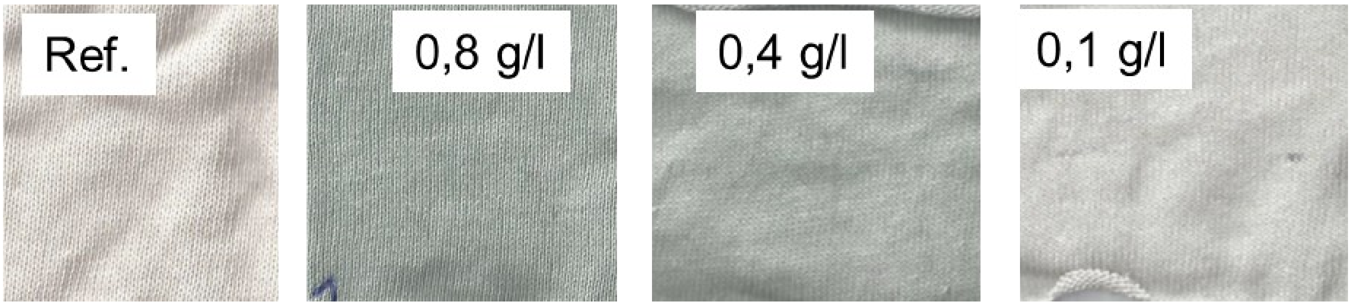

Fig. 6 Color impressions from Lyocell single jersey fabrics treated with organic IR absorber.

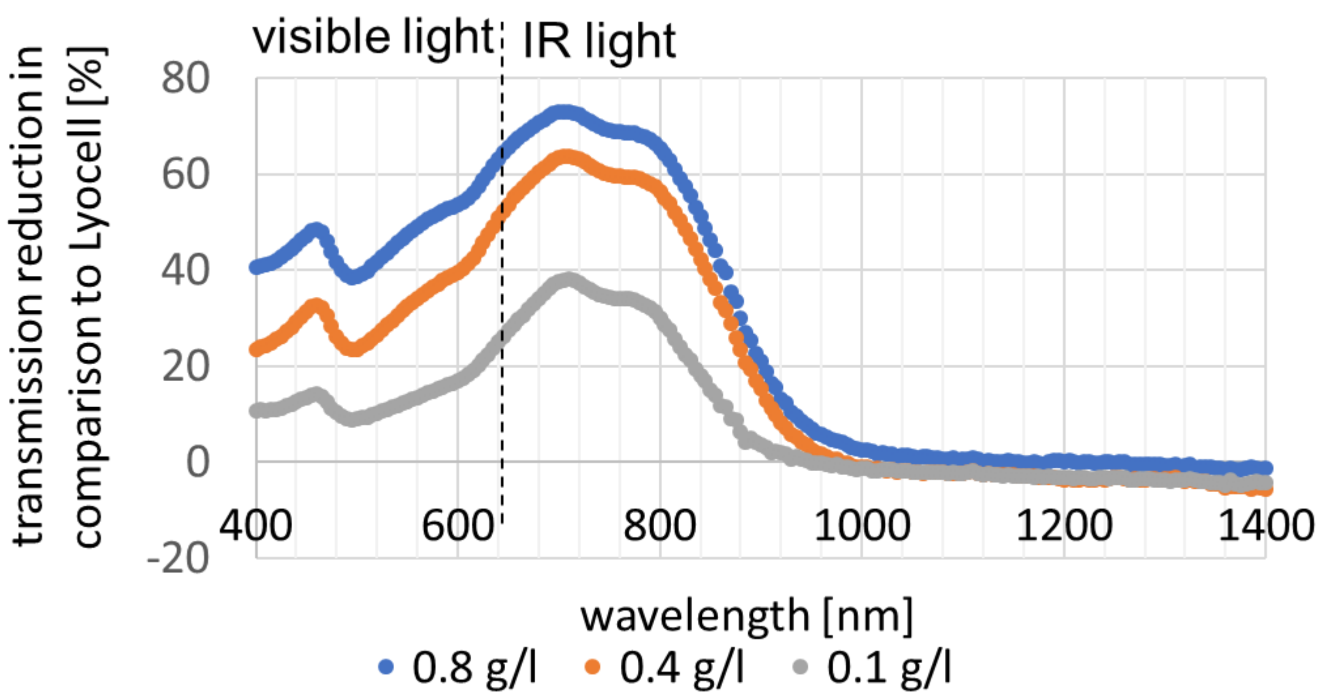

Fig. 7 Comparison of transmission reduction after treatment of a Lyocell fabric with the organic IR-absorber in increasing concentrations.

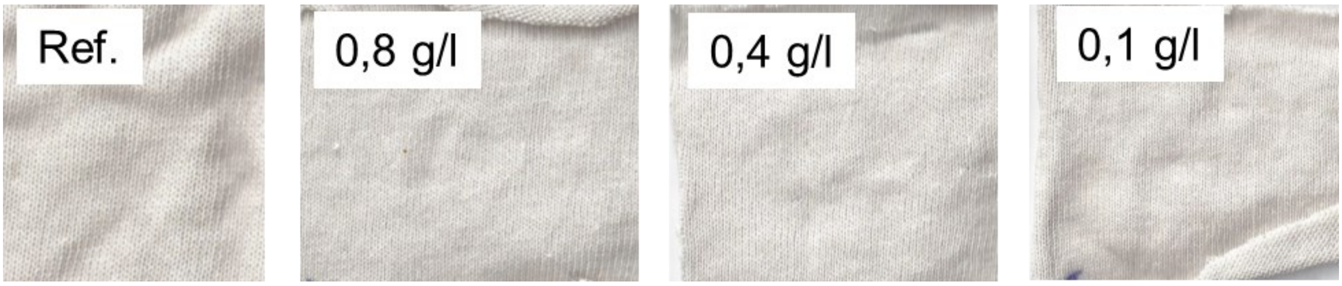

Fig. 8 Color impressions from Lyocell fabrics treated with hybrid absorber.

In contrast to the organic IR-absorber, the hybrid absorber leads to a totally different absorption behavior of the Lyocell fabrics (Figure 9). It should be remarked that an inorganic absorber may also increase the reflection of the material, this could lead additionally to its absorption to an increased reduction in light transmission. By application of the hybrid absorber in medium and high concentration, the optical transmission is decreased over the complete measured spectral range until 1400 nm (Figure 9), which is a significant advantage compared to the application of the organic IR absorber. However, the change in transmission with a maximum of 15% reduced transmission is significantly lower compared to the effects gained with the organic IR-absorber (cf. Figures 7 and 9). By application of the hybrid absorber in lowest concentration, an increased light transmission is gained. Such an increase could be explained by a change in textile structure or removing of other substances by the application of the hybrid absorber.

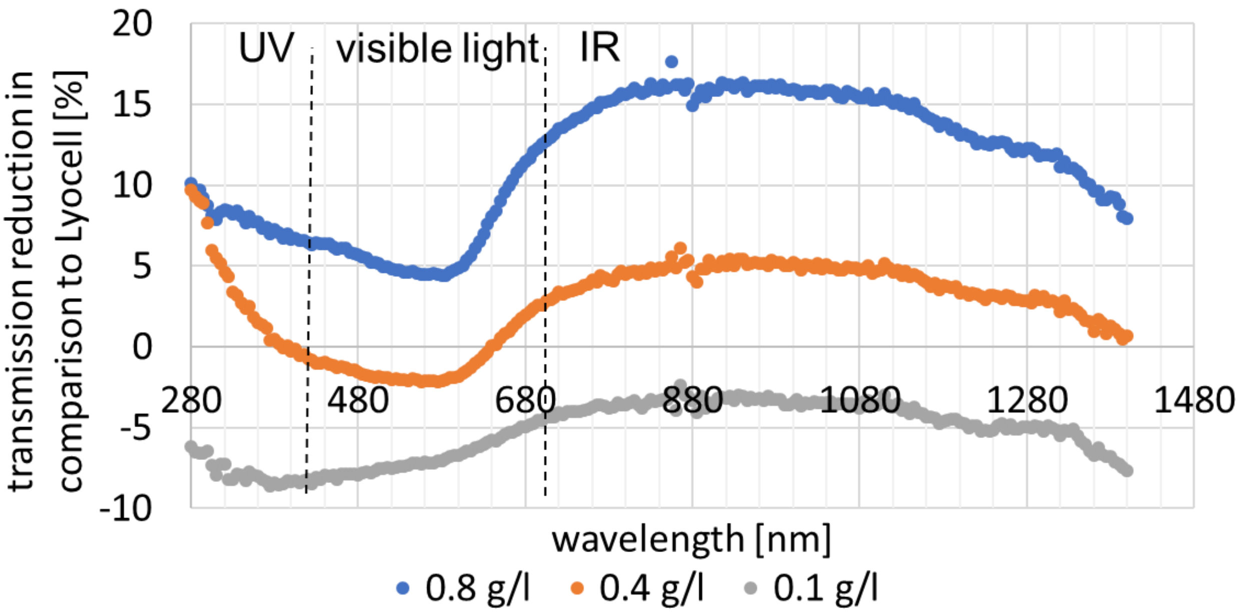

Fig. 9 Comparison of transmission reduction after treatment of a Lyocell fabric with the hybrid IR-absorber in increasing concentrations.

4 Conclusions

Functionalized Lyocell fibers containing TiO_2 reduce transmission in the UV range but have mainly no effect on infrared light. Dyeing with different dyes further reduces UV transmission and has a certain influence on infrared transmission. The application of IR absorbers on Lyocell textiles increases the protection against IR irradiation. However, one type of the evaluated IR absorbers is especially effective at IR light in the special range till 900 nm, while the other is also effective at IR higher wavelengths. In summary, several promising approaches to realize fabrics with reduced transmission for UV and IR light are evaluated. Areas of application for this kind of developed fabrics potentially arise in the fields of workwear, leisurewear, sportswear and kids wear, aiming in particular at the outdoor sector.

Author Contributions

K. Klinkhammer: experimental work (especially dyeing experiments), data evaluation and writing; K. Ratovo: experimental work (especially spinning and knitting) and data evaluation; O. Heß: experimental preparations and spectroscopic measurement; E. Bendt: supervision of experimental work (especially knitting and design); T. Grethe: data evaluation and main initiator of the related research project at Niederrhein University of Applied Sciences; M. Krieg: main initiator of the related research project at the TITK and supervision of experimental work (especially production of special fibers); M Sturm: experimental work (especially fiber production); T. Weide: supervision of experimental work (especially spinning and yarn production); B. Mahltig: main initiator of the related research project and current project leader, data evaluation and main writing of this paper.

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Conflicts of Interest

The authors declare no conflict of interest.

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