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The comfort properties of cosmeto-textiles functionalized with protein-based nanoemulsions encapsulating Vitamin-E

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ABSTRACT

The comfort properties of a textile cannot be dissociated from its function. Considering this premise, we evaluated the physical and mechanical performance of a previously developed cosmeto-textile composed of cotton/elastane, functionalized with bovine serum albumin (BSA) and BSA/silk fibroin (BSA/SF) nanoemulsions, encapsulating α-tocopherol (vitamin E). The surface functionalization of cotton fabrics with the nanoemulsions was confirmed by fabric staining with Coomassie Brilliant Blue R250 and by FTIR-ATR. The comfort properties including wetting, stiffness, stretching, draping ability, electrical resistance, and air and vapor permeability were evaluated. The results revealed that the functionalization of cotton fabrics with the developed protein-based nanoemulsions did not disturb the comfort properties of the textile material nor its functionality. This gives a good indication of the potential of the developed breathable cosmeto-textile to be used in contact with the human body with acceptable performance.

纺织品的舒适性与其功能是分不开的. 考虑到这一前提, 我们评估了先前开 发的由棉/弹性纤维组成的美容织物的物理和机械性能, 该织物具有牛血清 白蛋白(BSA)和牛血清白蛋白/丝素蛋白(BSA/SF)纳米乳液的功能化, 包封α-生育酚(维生素E). 通过考马斯亮蓝R250染色和FTIR-ATR分析, 证实 了纳米乳液对棉织物的表面功能化. 评价了织物的润湿性、刚度、拉伸 性、悬垂性、电阻、透气性和透气性等舒适性. 结果表明, 所研制的蛋白质 基纳米乳液对棉织物的功能化既不影响织物的舒适性, 也不影响其功能性. 这很好地说明了所开发的透气美容织物在与人体接触时具有可接受性能的 潜力.

KEYWORDS

Cotton; functionalization; nanoemulsions; vitamin E; comfort properties

关键词

棉花; 功能化; 纳米乳液; 维 生素E; 舒适性

Introduction

Textiles that possess skincare properties are usually called cosmeto-textiles (Muñoz et al. 2017). These textiles incorporate carriers with active substances, which are released depending on the external stimulus. The use of α -tocopherol as an active compound for the development of cosmeto-textiles has been assessed through different methodologies, including emulsification or micro-emulsion polymerization, interfacial or precipitation polymerization, emulsion evaporation, emulsion diffusion, solvent displacement, and salting out (Astete and Sabliov 2006). Microencapsulation is the most common and effective solution regarding the encapsulation of both hydrophobic and hydrophilic compounds (Ripoll et al. 2010). Several authors have been undertaking the encapsulation of α-tocopherol. Yenilmez et al. used chitosan (CS) microspheres to encapsulate vitamin E (α -TP) (Yenilmez,

Başaran, and Yazan 2011). The in vitro studies revealed a burst release from CS microspheres after 5 min of incubation with a complete release after 6 h. The *in vitro* antioxidant effect of the formulation, when evaluated by the DPPH test, revealed that CS could protect α-TP from degradation and its release from microspheres enhanced the moisture and the elasticity of the skin. Türkoğlu et al. used ethyl cellulose to prepare microcapsules containing α-TP through complex coacervation technique, and the padding method was used for application onto cotton fabrics (Turkoğlu et al. 2017). The authors confirmed the sustained release of α -TP from the produced microcapsules and its antioxidant activity. Alba and Banga entrapped vitamin E into nanostructured lipid carriers (NLCs) and nanoemulsions (NEs) (Abla and Banga 2014). They concluded that formulating tocopherol as NLCs could be beneficial to produce a stable, nonirritant, and aqueous formulation with antioxidant activity. Generally, the methodologies to apply microcapsules or microemulsions to the textiles include padding, coating, spraying, or immersion (Yılmaz and Öndoğan 2014). Among all, exhaustion bath and padding remained the preferred due to their simplicity and cost-effectiveness (Ripoll et al. 2010). Due to the weak adhesion of the particles onto the textile fiber surface, it is often essential to use a thermoplastic binder or adhesive (Ripoll et al. 2010). However, binders have poor resistance to washing, impairing a rough touch to the fabrics (Guignard et al. 2015; Ripoll et al. 2010). Therefore, it is imperative to find new alternatives of functionalization. A number of methods to create a covalent bonding between fibers and particles (organic or radical reactions, ozonization, and photochemistry) have been developed. Other techniques such as plasma and sol-gel are used to functionalize fabric permanently (Azizi, Chevalier, and Majdoub 2014; Ismail 2016; Luo et al. 2011; Mahltig 2008; Nadi et al. 2018; Ripoll et al. 2010; Rivero et al. 2015; Tavares et al. 2020; Yamato et al. 1993).

In a previous work, vitamin E was entrapped into NEs made by bovine serum albumin (BSA) and by BSA/silk fibroin (SF) via ultrasonic emulsification (Ghaheh et al. 2017a). Protein-based NEs incorporating vitamin E (α -tocopherol) in their composition were efficiently coated onto scoured cotton fabrics by pad-cure methodology. The release profile of vitamin E showed an initial burst in the initial time points reaching the stationary level of around 40% after 48 h of incubation. The effectiveness of the antioxidant activity was evaluated by ABTS free radical reduction, and the results show that all the coated samples presented antioxidant activity when compared with the noncoated fabrics.

So far, a large number of researchers have been focusing on the release behavior of core materials onto skin or on the sustainability of the microcapsules on the fabric (Ghayempour and Montazer 2016). However, only a few studies have mentioned the comfort properties of the final textiles functionalized with the developed microcapsules or microemulsions (Son, Yoo, and Shin 2014). Considering that the global performance of a textile product results from the combination of the functionality with the comfort aspects, it is imperative to evaluate the physical and mechanical behavior of the final products.

In the present work, BSA and BSA:SF nanoparticles containing α -TP were produced according to the method previously described (Ghaheh et al. 2017a, 2017b) and applied on knitted cotton/elastane fabrics without additional binders. The comfort properties of the functionalized fabrics, including stiffness, wetting, electrical resistance, stretching, air permeability, and mechanical properties, are evaluated.

Materials and methods

Materials and equipment

Unless otherwise stated, all the solvents and reagents used in this study were commercially supplied by Sigma-Aldrich and used as received. Cocoons were donated by Dr. Silvia Cappellozza from 'Sezione Specializzata per la Bachicoltura' (Padova). The experimental setup used for nanoparticles production included a probe-type ultrasound source (20 kHz Sonics & Materials Vibracell CV 33) fitted with a 3-mm-diameter titanium micro-tip. Power delivery was controlled as percentage amplitude (40%). The reaction vessel was an open glass cell (diameter 19 mm and height 75 mm) containing the sample

solution (10 mL). The sonochemical reactor temperature was controlled by a thermostatically controlled water bath equipped with a freezer exchanger spot within a thermojacket cell, which gave a constant operating temperature (10 ± 1 °C). The characteristics of bleached cotton fabrics used for the experiments were as follows: rib structure ($70 \cot /30 \text{ Lycra}$); ($12 \text{ wales} \times 19 \text{ course}$)/cm; 500 g/m^2 ; 28/11 Ne; thickness 0.52 mm.

Nanoparticles production, fabric functionalization, and characterization

The protein-based nanoparticles were prepared and characterized according to the methodologies previously described by Shahmoradi et al. (Ghaheh et al. 2017a).

Cotton samples were washed and functionalized according to the methodologies previously described by Shahmoradi et al. (Ghaheh et al. 2017b).

In order to confirm the presence of protein nanoparticles on the fabric, Coomassie Brilliant Blue R-250 was used for samples staining (Georgiou et al. 2008; Kruger 2009). All samples including the control (without protein) were stained with 0.5 g/L Coomassie Brilliant Blue at 60°C for 60 min. The samples were then washed with distilled water until the waste water was clear. Finally, the samples were dried at room temperature. To evaluate the adhesion of the nanoparticles to the fabric, the color absorption was calculated via Kubelka–Munk equation ($\frac{K}{S}$). Each sample was tested three times, and the mean was reported.

Fourier transform infrared spectroscopy (FTIR)

The chemical structure of control and functionalized samples was analyzed by FTIR using an IR spectrophotometer (Nicolet Instrument Corporation, Waltham, MA, USA). Scans were completed between 4000 and 450 cm⁻¹ at a resolution of 4 cm⁻¹. Baselines for each sample spectrum were normalized using spectrum software.

Wetting properties of functionalized fabrics

Water droplet absorption time was measured according to the BS4554 standard method. The samples were laid flat without any wrinkles on a horizontal surface and a droplet of stilled water (0.1 mL) was dropped on the sample from a height of 1 cm. Afterward, the time of complete water drop absorption was noted. The test was carried out 10 times in different areas of each specimen.

In order to measure the moisture regain, control and functionalized samples were firstly conditioned at room temperature for 24 h and weighed. Then, the samples were kept at 105°C for 1 h. Afterward, the samples were weighed and placed back in the oven and weighed again after 10 min. This procedure was repeated until a constant weight was reached. The moisture regain was then calculated by using equation (1):

$$R = \frac{W_w}{W_d} \tag{1}$$

where W_w is the weight of water remaining in the fabric and W_d is the weight of fabric after drying (Montazer, Keshvari, and Kahali 2016).

The water retention of the functionalized samples was measured according to ASTM D2402 standard method. Briefly, samples were individually floated in distilled water for 24 h. Then, each sample was centrifuged for 2 min at 7800 rpm, dried for 1 h at 105°C, weighed and placed back in the oven. The samples were then weighed every 10 min until a constant weight. The water retention value was calculated according to equation (2):

$$WRV = \frac{W_w - W_d}{W_d} \tag{2}$$

where W_w and W_d are the weights of fabric before and after drying, respectively. The vertical wicking of the functionalized samples was evaluated according to ATCC TM197 standard method. Samples with a dimension of 3×20 cm² were suspended in distilled water for 2 h at room temperature from the last 1 cm of their height. The wetting height of the samples was measured as a criterion for the vertical wicking (Montazer and Kahali 2016).

Mechanical properties of functionalized fabrics

In order to measure sample stiffness, the bending length was determined by a Shirley Fabric Stiffness Tester (Stiffness Tester, SDL, UK) according to ASTM D1388 method and using equation (3):

$$C = \frac{L}{2} \tag{3}$$

where *L* is the overhang length and *C* is the bending length.

Stretching percentage, maximum stretching percentage, and permanent stretching percentage of the control and functionalized samples were evaluated according to ASTM D3107 in both course and wale directions, and the results were obtained using equations (4–6):

$$Stretching(\%) = \frac{B - A}{A} \times 100 \tag{4}$$

$$Maximumstretching(\%) = \frac{C - A}{A} \times 100$$
 (5)

Permanentstretching(%)=
$$\frac{D-A}{A} \times 100$$
 (6)

where A is the distance between the upper and lower sections of the fabric (250 mm), B is the distance between two known marks on the fabric after applying the fourth tension (reported in mm), C is the distance between two known marks after suspending the sample for 30 min with a prescribed load (reported in mm), and D is the distance between two known marks after 2 h of relaxation.

The draping ability of the fabrics was assessed in a Cusick drapemeter following the BS 5058:1973: method for the assessment of drape of fabrics. A low drape coefficient indicates easy deformation of a fabric, and a high drape coefficient indicates less deformation.

Electrical surface resistivity of functionalized samples

Electrical surface resistivity of samples was tested according to AATCC Test Method 76-2005 by means of a static voltmeter (Static-Voltmeter R-4021, Zurich, Switzerland). The functionalized samples were cut into $10 \times 1~\text{cm}^2$ and placed in a firm contact with the voltmeter electrodes. A voltage of 50 V was applied, and the time for discharging was measured by a chronometer (Montazer, Ghayem Asghari, and Pakdel 2011). The resistance electrode is plugged into the grounding sockets of the input terminal, and the test specimen is clamped between the two spring clips. The insulated input terminal is then charged to 150 V by actuating the pushbutton, the discharge time is measured with a stop watch from this moment till the drop of the tension value to half value. The half value is marked on the galvanometer by a broken line and "R". This measuring method is known as the integration method. The surface resistance is determined as follows:

Measured time (in seconds)
$$\times 10^{11} = Resistance(inohms)$$
 (7)



Air permeability of functionalized samples

Air permeability was determined by applying a differential pressure to samples and measuring the airflow $(L/m^2/s)$ according to the procedure described in standard ASTM D737-96.

Water vapor transmission rate (WVTR)

The WVTR was tested using the upright cup test method according to GB/T 12704.2-2009 standard procedure. The samples were housed in an environmental chamber at the air temperature of $38 \pm 0.5^{\circ}$ C and relative humidity of 50%, and the air velocity was 2.8 ± 0.25 m s⁻¹. Circular specimens, 7.4 cm in diameter, were cut from each fabric and placed on an aluminum cup, which was filled with 34 mL of distilled water. The WVTR values were calculated from the change in the weight in the 2 h period using the following formula:

$$Q_{WVT} = \frac{\Delta W}{A_L} \tag{8}$$

where Q_{WVT} is the WVTR (g m² h⁻¹), ΔW is the change in the weight of the water sample contained in the cup, A is the test area of the specimens, and t is the time duration (in this case, t is 2 h).

Statistical analysis

Statistical analysis was carried out using a one-way analysis of variance combined with Tukey's post hoc tests. Differences were considered as significant when *p*-value <.05.

Results and discussion

Characterization of functionalized fabrics with nanoparticles

Cotton fabric samples were functionalized with the prepared NEs according to the methodology previously mentioned (Ghaheh et al. 2017a). The curing step was optimized aiming to increment the functionalization to ensure the highest amount of NEs at the fabrics surface. This processing condition is expected to interfere not only with the functionalization degree but also with the final comfort properties of the fabrics. Figure 1 shows the FTIR-ATR spectra and the staining results, which confirm the efficient functionalization of the fabrics with the protein-based NEs.

Coomassie Brilliant Blue R-250 reacts with the amine groups of the protein from NEs causing the staining of the samples with a dark blue coloration. Figure 1C shows the control (untreated) cotton/ Lycra-samples and the samples functionalized with NEs after staining with Coomassie Brilliant Blue R-250 at the same conditions (dye content, temperature, time, washing). The color difference between the samples confirms the presence of the protein at the fabric's surface. In addition, the effect of time and temperature of curing on the fixation of the nanoparticles was also studied by measuring the spectral value K/S. The results showed that there was a negligible difference between the samples cured at 50 and 100°C. The results also express the direct proportionality between the intensity of the staining and the amount of protein deposited at the fabric surface. The FTIR-ATR was also explored to confirm the presence of the NEs at the surface of the coated samples. The FTIR spectrum of the control fabric depicts the expected pattern (Gaspar. D, Fernandes. S N, et al. 2014), whereas the fabric functionalized with both BSA and BSA:SF NEs revealed a similar spectra, being the major peaks superimposed with the control. Given that the analysis was carried out directly in the structurally complex fabric, no major differences between samples were expected. Nonetheless, both functionalized fabrics showed a small peak at around 1750 cm⁻¹. This peak is attributed to the carbonyl groups (C=O), which is present in many amino acids of the proteins, confirming the functionalization of the

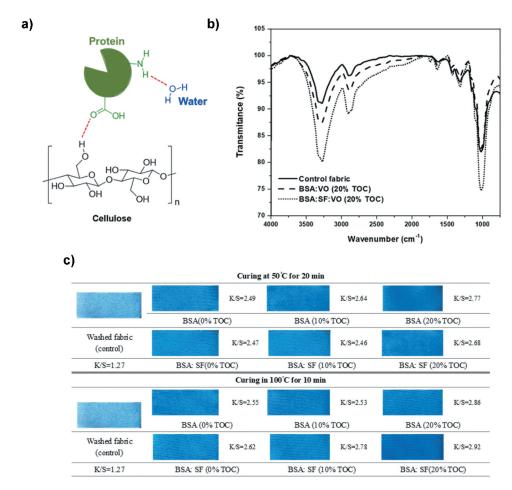


Figure 1. Confirmation of fabrics functionalization with protein-based nanoemulsions containing α -tocopherol: (A) representation of the interactions established between the nanoemulsions and the cellulose and the water; (B) FTIR-ATR of functionalized fabrics; (C) photographs of functionalized fabrics surfaces (the conditions of functionalization are reported in Ghaheh et al 2017b; the detection was performed by staining with Coomassie Brilliant Blue R-250, and the spectral values were evaluated after washing and drying).

fabric with the particles. We may also infer that the functionalization was even quite extensive, given the possible detection of an important functional group of the proteins by the FTIR analysis.

In Figure 1A, a scheme of the possible interactions between the cellulose of the fabric and the proteins from NEs is proposed. The interactions between fabric and NEs are expected to be established by hydrogen bonds.

Wetting properties of functionalized fabrics

Table 1 shows the results of water drop absorption of functionalized samples. According to the results obtained, the functionalization conditions, curing at 50°C for 20 min, promoted the highest impact on the absorption behavior of the fabrics, while the curing performed at 100°C for 10 min did not reveal significant effect on the time of water absorption (McClellan and Franses 2003). The samples functionalized under these curing conditions present a lower water drop absorption time (<40%) than control sample. From the results obtained, it is also possible to perceive that the composition of the NEs had no significant effect on the water drop absorption behavior of the fabrics.



Table 1. Water absorption time, moisture regain, water retention, and vertical wicking of functionalized samples with BSA-based and BSA/SF-based nanoparticles encapsulating vitamin E.

	Curing at 100 °C for 10 min				Curing at 50 °C for 20 min			
	Water drop absorption (s)	Moisture regain (MR %)	Water content (MC %)	Vertical wicking (cm)	Water drop absorption (s)	Moisture regain (MR %)	Water content (MC %)	Vertical wicking (cm)
Control fabric	210 ± 8.5	3.4 ± 0.1	1.1 ± 0.1	1.5 ± 0.1	210 ± 0.1	3.4 ± 0.1	1.1 ± 0.1	1.5 ± 0.1
Fabric (BSA: VO; 0% TOC)	215 ± 8.5	4.7 ± 0.3	0.6 ± 0.06	4.5 ± 0.5	83 ± 6.0	4.9 ± 0.2	1.6 ± 0.1	6.4 ± 0.4
Fabric (BSA:VO; 10% TOC)	198 ± 8.9	4.5 ± 0.2	0.8 ± 0.02	5.0 ± 0.5	75 ± 6.9	4.6 ± 0.3	1.8 ± 0.1	7.5 ± 0.5
Fabric (BSA:VO; 20% TOC)	214 ± 7.0	4.6 ± 0.2	0.8 ± 0.02	6.0 ± 0.5	90 ± 7.0	4.7 ± 0.2	1.9 ± 0.12	9.0 ± 0.2
Fabric (BSA:SF: VO; 0% TOC)	311 ± 8.4	4.4 ± 0.2	1.0 ± 0.12	3.0 ± 0.4	80 ± 5.8	4.6 ± 0.3	1.2 ± 0.08	5.0 ± 0.2
Fabric (BSA:SF: VO; 10% TOC)	306 ± 8.9	4.3 ± 0.2	0.9 ± 0.08	4.5 ± 0.4	78 ± 8.2	4.4 ± 0.3	1.4 ± 0.09	6.0 ± 0.5
Fabric (BSA:SF: VO; 20% TOC)	322 ± 5.4	4.3 ± 0.2	0.6 ± 0.02	5.0 ± 0.3	88 ± 7.3	4.5 ± 0.2	1.5 ± 0.14	8.0 ± 0.4

Note: VO: vegetable oil; TOC: tocopherol

The results of moisture regain of fabrics functionalized with protein-based NEs are also summarized in Table 1. The functionalization of the fabrics with BSA-based nanoparticles resulted in an increase of about 40% of the water regain compared to the control samples. When semicrystalline SF was incorporated in the NE formulation and cured under the same conditions, an increase of about 32% in water regain was observed. The presence of TOC as well as the curing conditions did not have a significant effect on the final moisture regain values.

The results revealed that the deposition of the protein-based NEs conferred an improved hydrophilic character to the cotton functionalized fabrics. Hydrophilic amino acids like glycine and serine from SF and the basic and acidic amino acids like aspartic acid, glutamic acid, lysine, and arginine from BSA can absorb moisture and increment hydrophilicity (Cavaco-Paulo and Gubitz 2003; Peters Jr 1985). Moreover, the presence of NEs can increase the fabrics' surface roughness and thus retain moisture (Hearle and Morton 2008; Spahr and Edsall 1964). The higher curing temperature (100°C) is expected to denature proteins and hence contribute to the decrease of about 3–4% of the moisture regain.

The results of water retention are also shown in Table 1. As indicated in the table, and in agreement with the previous data, the curing conditions played a significant role in the final behavior of water retention. Functionalized samples cured at 50°C for 20 min were able to retain more water molecules than control or functionalized samples cured at 100°C for 10 min.

The protein composition and consequently the hydrophilic sites at the fabrics' surface promoted deeper penetration of the water molecules due to the formation of hydrogen bonding between the water molecules and the hydrophilic groups of the protein side chains (Zayas 1997) (Figure 1A), limiting the water molecules to escape from the sample. Moreover, under these curing conditions (50° C for 20 min), the water retention by samples functionalized with BSA-based NEs was significantly higher than that of samples functionalized with BSA/SF-based NEs, which can be attributed to the amorphous structure of BSA that may increase the water retention capacity.

Denaturation caused by the curing high temperature results in the unfolding of the polypeptide chains and in the transition of the globular conformation to a random coil that can reduce the available polar amino acid groups to bind water (Zayas 1997). On the other hand, denatured NEs acted as a retardant film limiting water absorption and thus less water could penetrate to the fabric structure.

Water-transferring mechanism in fabrics is similar to liquid wicking in capillary tubes. Capillary action is determined by the diameter and the surface energy; the smaller the diameter or the higher

surface energy, the highest is the capillary action. Narrow space among fibers causes more water to be wicked in the fabric (Montazer and Kahali 2016; Saville 1999).

Functionalizing cotton/Lycra by depositing protein-based NEs among fibers generated small diameter spaces with high surface energy, leading to a significant increase in capillary action. Vertical wicking of the fabric is a function of capillary movement of water through fabric. The presence of NEs at the surface increased the surface roughness endowing samples with higher surface energy. Therefore, as indicated in Table 1, an increase of about six and fivefold of the vertical wicking values was observed for fabrics functionalized with BSA-based and BSA/SF-based NEs, cured at 50°C for 20 min, respectively, compared to the control sample. Both BSA and BSA/SF samples cured at 100° C showed lower vertical wicking, which may be attributed to the reduced polar amino acid groups available for water binding. Nevertheless, samples cured at high temperature, 100°C, still presented high values of vertical wicking due to the nanoscale roughness formed by the presence of NEs at the fabric's surface.

Mechanical properties

Fabric stiffness is an important characteristic determining the tactile property of a fabric and can be defined as the opposite of stiffness, which is measured by the bending length. The higher the bending length, the stiffer is the fabric (Shiddique, Repon, and Mamun 2019). The effect of the protein NEs (with and without α -TP) on the bending length of functionalized cotton samples was evaluated, and the results are shown in Figure 2. As depicted, the functionalization of the fabrics increased significantly (p < .05) the bending length where an average increase of about 15% and 38% was observed for samples functionalized with BSA-based and BSA/SF-based NEs, respectively, compared to the control samples. The increase of TOC content in the NEs does not significantly (p > .05) increase the bending length.

Protein-based NEs are deposited at the fabrics' surface and between yarns and fibers establishing hydrogen bonding between them. The high volume of NEs may be an obstacle for fabric bending leading to an increase in bending length. Moreover, the high molecular weight of SF and BSA may induce the formation of a film at the moment of NEs deposition, causing the increase in the fabrics' stiffness. As shown in Figure 2, a slight decrease in the flexibility may be related to an increase of the surface friction after coating (Gupta, Chaudhary, and Gupta 2015). However, the presence of TOC in

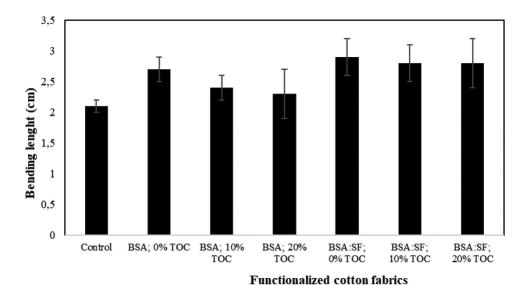


Figure 2. Bending length of control and functionalized cotton samples.

the NEs seems to counteract this tendency by increasing the flexibility due to its plasticizer role. Nevertheless, the presence of SF within nanoparticles has reduced, still not significantly, the plasticizing effect caused by the presence of TOC. The lower flexibility of samples functionalized with BSA/SF-based nanoparticles can arise from the high molecular weight, on the one hand, and the semi-crystalline structure of SF, on the other hand.

Table 2 presents the values of stretching of cotton samples after functionalization with the developed NEs (BSA:SF; 20% TOC). Statistical analysis of the results revealed that no meaningful difference of the stretching properties is observed for the functionalized samples in comparison to the control. Control samples stretched 28.6 \pm 4.1% in course direction, suffering a slight decrease to 24.8 \pm 2.9% after functionalizing with BSA:SF:(20%TOC) NEs (Table 2). A similar trend was observed for the permanent stretching. In the course direction, it decreased from 50.3 \pm 1.5% for control samples to 47.8 \pm 4.0% for samples functionalized with BSA:SF(20%TOC) NEs. This can be due to SF structure, which is predominantly comprised by β -planes that may hinder the flexibility of the fibers. Moreover, hydrogen bonding between protein NEs and their high molecular size and volume may cause less flexibility to the functionalized samples. The increase of surface friction is considered to play the main role in decreasing the fabric flexibility (Gupta, Chaudhary, and Gupta 2015).

Fabric drape is the ability of a fabric (circular specimen of known size) to deform when suspended under its own weight in specified conditions. Draping ability of a fabric is a combined effect of several factors such as stiffness, flexural rigidity, weight, thickness, etc. This factor, together with fabric stiffness and stretching ability, will determine the comfort properties of the final products, being though fundamental is its prediction. Considering that the fabrics become stiffer after functionalization, we expected a slight decrease in the fabric drape coefficient, which is confirmed by the results obtained after functionalization (Figure 3). The decrease was more pronounced for the samples functionalized with the NEs containing both BSA and SF proteins, and accompanies the increase in

Table 2. Stretching, maximum stretching, and permanent stretching of control sample and samples functionalized with BSA:SF (20% TOC).

Sample	Measuring direction	Stretching (%)	Maximum stretching (%)	Permanent stretching (%)
Control sample	Course	28.6 ± 4.1	69.7 ± 4.6	50.3 ± 1.5
	Wale	9.1 ± 0.9	18.2 ± 2.8	13.6 ± 1.8
Fabric (BSA: SF:20%TOC)	Course	24.8 ± 2.9	75.5 ± 3.9	47.8 ± 4.0
	Wale	9.6 ± 1.3	11.4 ± 1.2	13.2 ± 1.6

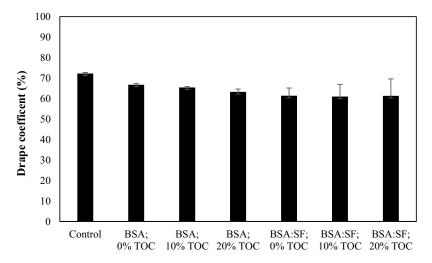


Figure 3. Drape coefficient of control and functionalized cotton samples.

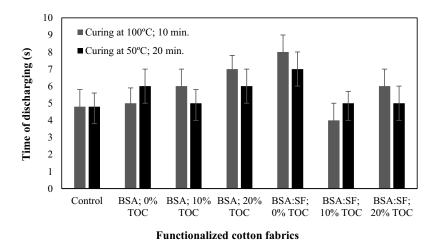


Figure 4. Time of discharge of control and functionalized cotton samples.

fabrics' stiffness. The changes observed are not that drastic that would disturb the comfort properties of the fabrics as it will be confirmed further by the air and water vapor permeability results.

Electrical surface resistivity

The surface resistivity defines a fixed surface length's electrical resistance on an insulating material. Figure 4 illustrates the results of static electrical discharge time of functionalized samples in comparison to control sample.

There was a significant difference between the time of discharge for the control and functionalized samples. Moisture has an inevitable effect on the antistatic properties of the fabrics. Resistivity of the fibers is affected by moisture regain resulting from the polar groups of the proteins' molecular chains. The higher is the moisture regain, the lower is the resistivity and the time of discharging. In fact, water absorption drastically affects static electrical conductivity. Water is a suitable element for electrical loads transmission and facilitates ion migration.

The antistatic characteristics of the functionalized samples were enhanced significantly (88%) due to the increase of water absorption and moisture regain (Hearle and Morton 2008; Ngo and Bechtold 2017; Saville 1999).

Air and water vapor permeability

The breathability of a fabric is of great importance and can be altered negatively by coating. Therefore, air and vapor permeability of fabrics was measured before and after functionalization (Figure 5). The air permeability of control samples was initially $90.8 \pm 8.5 \text{ L/m}^2/\text{s}$ decreasing significantly after coating (p < .05) due to the filling of the gaps between fibers and yarns by NE deposition. The reduction of the air permeability (35%) of fabrics cured at 100°C for 10 min was greater than the reduction observed for fabrics cured at 50°C for 20 min (28%). However, the statistical analysis indicated that neither the presence of TOC within NEs nor the composition of the NEs influenced the airflow barrier property significantly (p > .5). The same tendency is observed for the water vapor results, being detectable a decrease of this property after fabrics' functionalization, comparatively to control samples. Considering the improvement of the hydrophilic properties of the fabrics, derived from the coating of the protein in the inter-spaces between fibers and yarns, it was expected that this property would not be disturbed to values considered limit for textile usage. It is also noteworthy that the water vapor transport

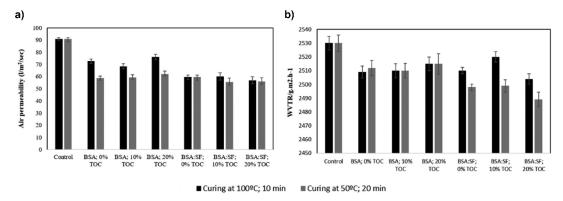


Figure 5. Air (a) and vapor (b) permeability of control and functionalized cotton samples.

through the microporous fabric employs much more complex mechanisms than air permeability. The air permeability takes place in convection conditions, where larger surface of clearance is good for air transmission. While water vapor permeability takes place in conditions of free convection, which is governed not only by porosity and pore diameter, but also by its base fiber moisture properties and the molecular mechanism (Fick's law), and is also depending on the capillary action (Wu Jingxia, Li, Jingye et al. 2015). Taking into account these assumptions, and despite the smaller surface available for air transmission and lower porosity (data not shown), derived from yarn interspaces protein filling, the moisture properties of the functionalized samples were improved (Table 1). These events might be responsible for the lower decrease of the air and water vapor permeability.

Conclusions

Cotton fabrics were functionalized with previously developed protein-based NEs made up of BSA and BSA/SF, containing different amount of α -tocopherol. The method of fabrics functionalization was based on pad-cure coating using different curing time and temperature, as previously reported by us. The efficacy of the coating in terms of antioxidant activity was already established; however, the comfort properties of the functionalized fabrics were not considered in the previous study. The comfort properties cannot be dissociated to the function and for this they were herein investigated. The results obtained allowed us to conclude that the curing temperature had a significant role on the final comfort properties of functionalized fabrics. High temperatures may lead to protein denaturation and consequently to a decrease of the surface energy of the samples. Low temperature of curing (50°C) was efficient to attain a functionalized fabric with greater water absorption and moisture regain. Functionalized samples subsequently exhibited improved antistatic characteristics. A slight decrease of the flexibility of the fabrics was observed after functionalization with NEs, although insufficient to impart rigidity and stiffness to the fabrics.

Moreover, the combination of the properties, air and water vapor permeability, despite the decrease observed after functionalization, is still acceptable to consider the substrates breathable and comfortable fabrics to be used as dressing materials.

The pad curing of cotton fabrics with BSA- and BSA/SF-based NEs containing vitamin E can impart antioxidant activity to the fabrics while maintaining their physical and mechanical properties without compromising the comfort properties, essential for materials to be used in contact with human body.

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