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Highlights:

- Antimicrobial functionalization of textiles is a pivotal factor for sustainability
- Antimicrobial finishing characterization in three different types of elastic bands
- Antimicrobial performance of two agents against three microorganisms
- Washing fastness analyzed for up to 50 washing cycles • Elastic bands mechanical properties were assessed

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Elastic bands antimicrobial functionalization

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Keywords: antimicrobial, functionalization, elastic bands, functional textiles

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Abstract

Sustainability of textile products encompasses the extension of their useful life period during which they adequately serve their intended purpose. Antimicrobial finishings can prevent microbial damage and extend textile lifespan. Even though the functionalization and characterization processes have been thoroughly described for woven, knitted and non-woven textiles, there is a lack of information regarding elastic bands or elastic straps. These materials comprise notable concentrations of elastane (EL). Here, three elastic bands: woven flat (WF), knitted flat (KF) and braided (BD), were functionalized using two commercial antimicrobial finishings: RUCO-BAC AGP (RUCO-BAC) and FRESH EF 4850 (FRESH). Elastic band mechanical properties were assessed up to 50 washing cycles (wc). Interestingly, the tensile strength performance was only clearly impacted in WF elastic bands. Elongation was enhanced after functionalization, and no obvious loss of elongation was observed, even after 50 wc. Elasticity recovery (E_R) was almost ubiquitously affected after functionalization with both antimicrobial finishing products, in particular after 50 wc. Nevertheless, all E_R values were above 70%. Weak decontaminate to moderate disinfectant activity was observed in pristine elastic bands against the tested microorganisms: MS2 bacteriophage, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. However, it was inexistant after a single wc, thus it was hypothetically attributed to paraffin applied during the knitting process. Elastic bands functionalized through padding using RUCO-BAC displayed moderate against MS2 and *S. aureus*. Its washing fastness was excellent

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against MS2, exhibiting a nearly constant activity after 1, 5, 10 and 20 wc. However, its activity against *S. aureus* and *P. aeruginosa* was seriously hindered after a single wc.

1. Introduction

Textile industry is under social pressure to implement cleaner and sustainable practices [1]. Consumer behavior is increasingly conscious of sustainability, with nearly 80% of the individuals scrutinizing the brands' labels for environmental clues. In addition, approximately 50% of consumers consider textile certifications useful. Textiles per se represent a highly relevant environmental issue [2]. Globally, at least 92 million tons of textile waste are discarded each year, of each approximately 73% end up in landfills [3-8].

A strategy to mitigate textile waste is to extend their durability. Nevertheless, microbial contamination reduces textiles lifespan.

A plethora of microorganisms can thrive in natural, artificial and synthetic textiles. The main issues that may arise from microorganism contamination, include: textile damage and/or consumption, bad odor generation, and potential health risks to the users [9]. A multitude of microorganisms possess the required enzymatic machinery to use natural and artificial textiles as nutrient sources, hindering textiles mechanical properties and shortening the garments useful lifespan.

Undergarments and garments that are in direct contact with the user's skin are extensively inoculated with the microbial flora present on the surface of the skin. These inocula tend to thrive in the presence of water and nutrients from sweat, inevitably increasing the number of washing cycles (wc) required for their elimination [10]. The number of wc represent a detrimental factor for the life span of a textile product [11]. The wc hinder properties, such as: tear and wear (fiber damage), shrinkage, loss of softness, lint formation, color fading, loss of breathability and repellency. Furthermore, it is widely recognized the release of microplastics from synthetic fibers during wc [12, 13]. In addition, the increasing application of polyfluoroalkyl substances (PFAS) finishings are recalcitrant and extremely health hazardous finishings [14], that may be released during the wc.

Finally, textiles may also serve as vehicles for pathogenic microorganisms [15]. Therefore, extensive research in functionalization processes is being performed in woven, knitted, or non-woven fabrics using commercial and novel antimicrobial agents [16]. However, the available

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literature on the functionalization and characterization using antimicrobial finishings of elastic bands is scarce [17].

Elastic bands are characterized by unique stretch and recovery properties provided by a relevant concentration of elastic fibers such as elastane (EL). EL is a synthetic fiber made from a segmented polyurethane comprising hard and soft segments, namely diisocyanate and monomers rich in hydroxyl groups, respectively [18, 19].

Elastic bands may comprise 5 to 30% (w/w) of EL. The elastic bands are required for the adequate and comfortable fitting of undergarments and garments, namely: brasserie straps, sports garments, winter garments, activewear, waistbands, cuffs, swimwear, among others. These garments are highly susceptible to microorganisms' contamination. Thus, the commercial finishing RUCO-BAC AGP (RUCO-BAC) has been described as an adequate finishing to provide antibacterial protection in different textile substrates architectures. Encompassing: nonwoven polypropylene (PP) [20], 100% cotton (CO) woven fabric [21, 22], knitted polyamide (PA)-polyurethane fabric [23], and even in CO, viscose (CV) and polyester (PES) [24]. However, to the authors knowledge there are no reports of its use for functionalizing textiles containing a high percentage of EL, such as elastic bands. In fact, these highly elastic fabrics have only been functionalized with antibacterial agents, such as calcium chloride (in CO-EL and PA-EL substrates), and quaternary silane compounds (in CO and CO-EL fabrics) [25, 26]. Therefore, due to the existing knowledge gap regarding the functionalization of these elastic materials using either RUCO-BAC and FRESH EF 4850 (FRESH), their application using common textile functionalization processes was evaluated. RUCO-BAC and FRESH comprise distinct antimicrobial agents and both are described as exhibiting good washing fastness. Thus, their use is intended to unveil their performance in poorly studied substrates towards a bacteriophage, a Gram positive and a Gram negative bacterium.

2. Materials and Methods

Three elastic bands (Table 1) and two antimicrobial agents (Table 2) were tested. The elastic bands woven flat (WF), knitted flat (KF) and braided (BD) were kindly supplied by Nastrotex – Industria de Passamanarias Lda (Porto, Portugal). The antimicrobial agent RUCO-BAC was obtained from RUDOLF – Produtos Químicos, S.A. (Porto, Portugal) and FRESH from Aquitex – Acabamentos Químicos Têxteis, S.A. (Porto, Portugal). In addition, the polymeric resin FRESH BZ1 BINDER (BZ1) from Aquitex was also used, being recommended to enhance washing fastness of FRESH. This is a cationic water soluble formulation with a pH of approximately 5. The tested

concentrations of RUCO-BAC and FRESH were used as detailed in the technical sheet of the finishing products.

Table 1. Elastic bands details.

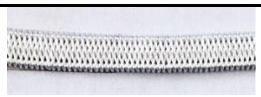
Elastic band image			
Structure	Woven flat (WF)	Knitted flat (KF)	Braided (BD)
Fabrication technology	Weaving	Knitting	Braiding
Composition % (w/w)	78 PA 22 EL	62 PES 38 EL	88 PA 12 EL
Width (mm)	10	5	3
Weight (g m^{-1})	1.8	2.4	1.6

Table 2. Properties of antimicrobial products.

Antimicrobial agent	RUCO-BAC AGP (RUCO-BAC)	FRESH EF 4850 (FRESH)
Description	Antimicrobial for all types of fibers	Antimicrobial for all types of fibers
Composition	Inorganic salts, titanium dioxide, silver chloride, surfactants	Quaternary ammonium silane derived from coconut extract
Application process	Exhaustion and padding	Exhaustion (not applicable to synthetic fibers) and padding
Other properties	Milky white Easily dispersible in cold or warm water pH 7.0 Anionic High washing fastness	Yellowish Water-soluble pH 5.5 Cationic Excellent durability
Maximum recommended concentration (g L^{-1})	5	10

2.1. Functionalization process

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The functionalization processes were performed after one wc according to the International Organization for Standardization (ISO) 105-C06:2010 C1S. Briefly, the elastic bands were washed with European Colourfastness Establishment (ECE) phosphate reference detergent (B; 4 g L^{-1}), at 60 °C for 30 min, using 25 metallic spheres, in a 50 mL bath at pH 10.5 (adjusted with 1 g L^{-1} of sodium carbonate). Subsequently to the wc, the elastics bands were rinsed twice for 1 min, using 100 mL of distilled water at 40 °C and dried at 50 °C overnight. The antimicrobial finishing of RUCO-BAC was performed through exhaustion or padding (RUCO-BAC_E and RUCO-BAC_P, respectively). According to manufacturer FRESH can be only applied through padding (FRESH_P). Elastic bands comprising 20 cm length in their relaxed state were subjected to each functionalization method. A schematic of the functionalization processes is shown in Figure 1.

2.1.1. Exhaustion

Elastic bands functionalized through exhaustion process encompassed the following conditions: RUCO-BAC concentration 5 g L^{-1}, liquor ratio of 1:10 (v/v), pH adjusted between 4.4 and 5.0 using acetic acid (0.5 M), for 30 min at 50 °C using Ibelus C-720 dyeing equipment (Pregitzer Lda., Guimarães, Portugal). Afterwards, the samples were collected and dried at 110 °C.

2.1.2. Padding

Elastic bands functionalized using padding technology comprised RUCO-BAC or FRESH at 5 g L^{-1} and 10 g L^{-1}, respectively. The padding mangle (Padder BHP, Roaches, United Kingdom) was initially adjusted to a liquor pick-up of 60%. Then, samples were immersed in the solutions for 5 min and padded at a pressure of 4 bar and velocity of 4 m min^{-1} at room temperature (approximately 21 °C). Afterwards, all samples were dried at 110 °C for 30 min. Samples functionalized with FRESH were also thermoset at 160 °C for 3 min. FRESH initial solution also contained 15 g L^{-1} of commercial binder compound BZ1.

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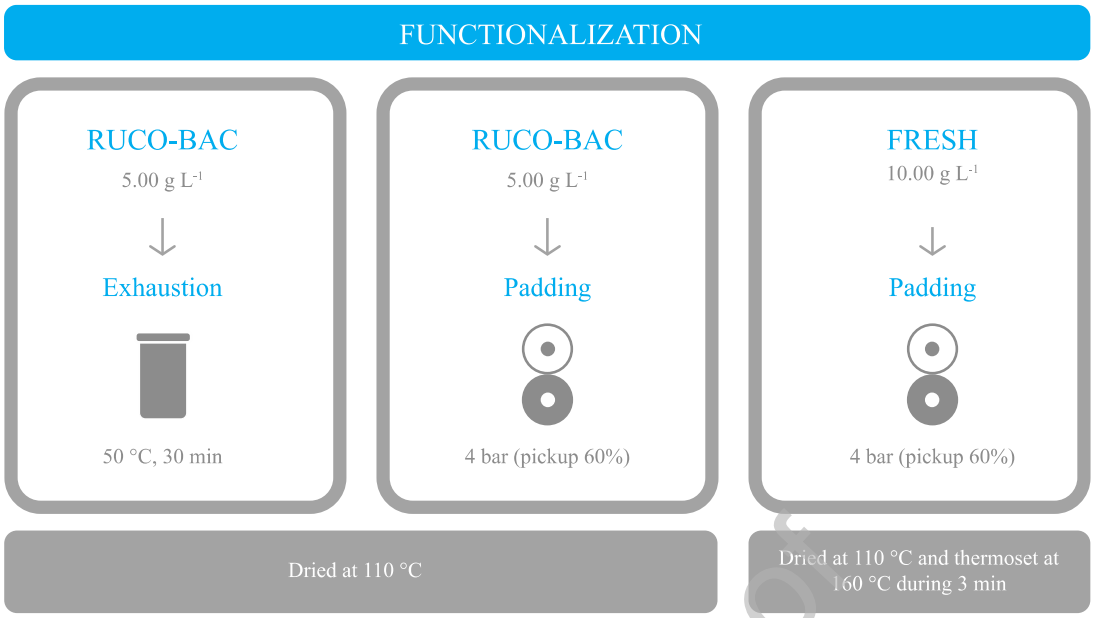


Figure 1. Schematics of functionalization processes.

2.2. Scanning electron microscopy

Elastic bands morphological analyses were carried out by scanning electron microscopy (SEM) with an ultra-high resolution field emission gun (FEINova 200, Mahwah, NJ, USA). Prior to morphological analyses samples were coated with a film of Au-Pd (80-20% w/w) of 50 nm, using a high-resolution sputter coater, 208HR Cressington Company, coupled to a MTM-20 Cressington High Resolution Thickness Controller (Cressington, Liverpool, UK). Sample topographical imaging was obtained using a secondary electron detector at a tensile acceleration of 10 kV.

2.3. Water contact angle

Water contact angle (WCA) was determined through static sessile drop method using 5 µL droplets of ultrapure water at room temperature (Data Physics OCA20, Filderstadt, Germany). A minimum of 10 measurements were performed in different areas of the samples. The graph was obtained using Prism 9 (GraphPad, version 9.0.0).

2.4. Washing fastness

Washing fastness evaluations were carried out after 1 and 50 wc. The first wc followed ISO 105-C06:2010 C1S standard. After each wc, the elastics bands were rinsed twice for 1 min in 100 mL

of distilled water at 40 °C. Then, the elastic bands were dried overnight at 50 °C. The following wc were performed using ISO 105-C06:2010 C1M standard. This method explores a more intensive washing, as it uses ECE detergent (4 g L^{-1}), at 60 °C for 45 min, and 50 metallic spheres in a 50 mL bath at pH 10.5 (adjusted with 1 g L^{-1} of sodium carbonate).

2.4.1. Dimensional stability

Standard ISO 5077:2007 was followed to determine the dimensional change of the elastic bands during washing and drying. Five replicates of each sample were placed on a horizontal table, without any tension, and their length was measured. Their percentage of dimensional variation was calculated by the equation (1). The exhibited plot was obtained using Prism 9 (GraphPad, version 9.0.0).

$$\mathrm{DV}(\%) = \frac{(\mathrm{Lf}-\mathrm{Li})}{\mathrm{Li}} \times 100 \mathrm{DV}\ (\%)\ (1)$$

where, DV is the dimensional variation, Lf is the final length displayed by the sample and Li is the initial size of the elastic bands.

2.4.2. Mechanical properties

A dynamometer Hounsfield H10KS (Redhill, UK) was used to analyze the mechanical properties of the elastic bands according to the American Society for Testing and Materials (ASTM) D 5035-11 (2019) standard with a single adaptation in the distance between the jaws. The percentage of elongation at break and the maximum force of each elastic band were determined. Five replicates of each sample were tested. The distance between the jaws was 10 cm, a preload of 2 N was set and a loading rate of 100 mm min^{-1} was used.

The same equipment and setup were used to access the percentage of elasticity recovery according to the British Standard (BS) EN ISO 20932-1. Ten cycles were performed in three replicates of each elastic band. In addition, after analyzing the behavior of the samples in the test of resistance to maximum force and elongation at break, an extension of 100% was defined for WF and BD, and of 50% for KF.

The dimension of each sample was verified once the test was completed and after 1 min, 10 min and 24 h. Equation 2 was used to estimate the percentage of elongation recovery (equation 2):

$$\mathrm{E_t}\ (\%) = \frac{(\mathrm{Lf_t}-\mathrm{Li})}{\mathrm{Li}} \times 100\ \ (2)$$

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where, E_t is the percentage of elongation recovery at time t, Li corresponds to the initial length, Lf_t is the length after removal from the dynamometer: 0 min (immediately after), 1 min, 10 min and 24 h.

Finally, the percentage of elasticity recovery (ER%) at times 0, 1 min, 10 min and 24 h was given by equation 3.

$$\mathrm{ER}(\%) = 100\% - \mathrm{E_t}(\%) \quad (3)$$

The graphs were generated using Prism 9 (GraphPad, version 9.0.0).

2.5. Antimicrobial analysis

2.5.1. Microorganisms and culture media

The Gram positive bacterium *Staphylococcus aureus* American Type Culture Collection (ATCC) 6538 and the Gram negative bacterium *Pseudomonas aeruginosa* ATCC 27853 were used for the antibacterial assessment. The antiviral properties were determined using bacteriophage MS2 ATCC 15597-B1, and the bacterium *Escherichia coli* ATCC 15597 as its host.

S. aureus was cultured in tryptone soy broth (TSB) and tryptone soy agar (TSA), as liquid and solid media, respectively. *P. aeruginosa* was grown in nutrient agar (NA) and nutrient broth (NB). These culture media were purchased from Liofilchem (Teramo, Italy). *S. aureus* and *P. aeruginosa* were transferred and diluted in phosphate buffer saline (PBS, 8 g L^{-1} of sodium chloride (Merck KGaA, Darmstadt, Germany), 0.2 g L^{-1} potassium chloride (Panreac, Barcelona, Spain), 1.44 g L^{-1} of disodium phosphate (Fisher Scientific, Hampton, USA) and 0.24 g L^{-1} potassium dihydrogen phosphate (Sigma-Aldrich Química S.L., Lisboa, Portugal), pH 7.4). MS2 bacteriophage and its host were maintained, transferred, diluted, and cultured in ATCC 271.

2.5.2. Antimicrobial quantification

The antimicrobial efficacy of the elastic bands was evaluated through the adaptation of one standard for bacteria (American Association of Textile Chemists and Colorists (AATCC) test method 100-TM100 [27]) along with the merging and adaptation of two standards AATCC 100-TM100 and ISO 18184:2019 [28] for the bacteriophage as described in [29, 30]. Briefly, a pre-inocula of *S. aureus*, *P. aeruginosa* and *E. coli* (host) were prepared in 25 mL of corresponding liquid media and incubated for 12 h at 37 °C and 120 rpm. In addition, a previously prepared MS2 bacteriophage inoculum containing 1×10^7 plate forming units (PFU) mL^{-1} was maintained at 4 °C until further use. The samples, with 2.5 cm length, were inoculated with 50 µL containing 1×10^7 colony forming units (CFU) mL^{-1} of *S. aureus*, and *P. aeruginosa* 1×10^7 PFU mL-1 in ATCC

271, for 1 h or 2 h for MS2, at room temperature. The samples were then immersed in 5 mL (PBS for bacteria or ATCC 271 medium for MS2) and thoroughly vortexed for at least 1 min. The washing liquid was serially diluted in PBS for bacteria or ATCC 271 for MS2, and subsequent dilutions were inoculated in solid medium. For MS2, the Petri dishes containing culture ATCC 271 medium were previously inoculated with 1 mL of 1×10^{9} CFU mL^{-1} of *E. coli* host. The Petri dishes were incubated, and CFU and PFU were counted after 20 h at 37 °C. The concentration was estimated, and the log reduction was calculated according to equation 4:

$$\text{Log reduction} = \text{Log[i]} - \text{Log[f]} \quad (4)$$

where Log[i] corresponds to the inoculum concentration for each microorganism and Log[f] is the concentration after contact with the elastic bands. All plots were generated using Prism 9 (GraphPad, version 9.0.0).

2.6. Fourier-transform infrared spectroscopy attenuated total reflection

A paraffin roll commonly used in the textile industry for lubricating yarns during weaving and knitting was analyzed through Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) in a Shimadzu IRAffinity-S1 (Kyoto, Japan). The obtained spectrum covered a wavenumber between 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 125 scans were performed. The graph was generated using Prism 9 (GraphPad, version 9.0.0).

2.7. Statistical analysis

All results are displayed as average and standard deviation. All data sets were tested to verify their compliance with the required prerequisites for parametric statistical analysis. Shapiro-Wilk tests were performed to verify data Gaussian distribution. When the data complied with the pre-requests for a parametric analysis, one-way analysis of variance (ANOVA) followed by Dunnett's multiple comparison, were performed. Control of each type of elastic band was used as standard for the multiple comparisons. The p-value used was defined as < 0.05. The antimicrobial analysis were not subjected to statistical analysis due to their inherent impossibility to comply with parametric analysis pre-requisites.

3. Results and discussion

3.1. Scanning electron microscopy

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The SEM images of the functionalized elastic are present in Figure 2.

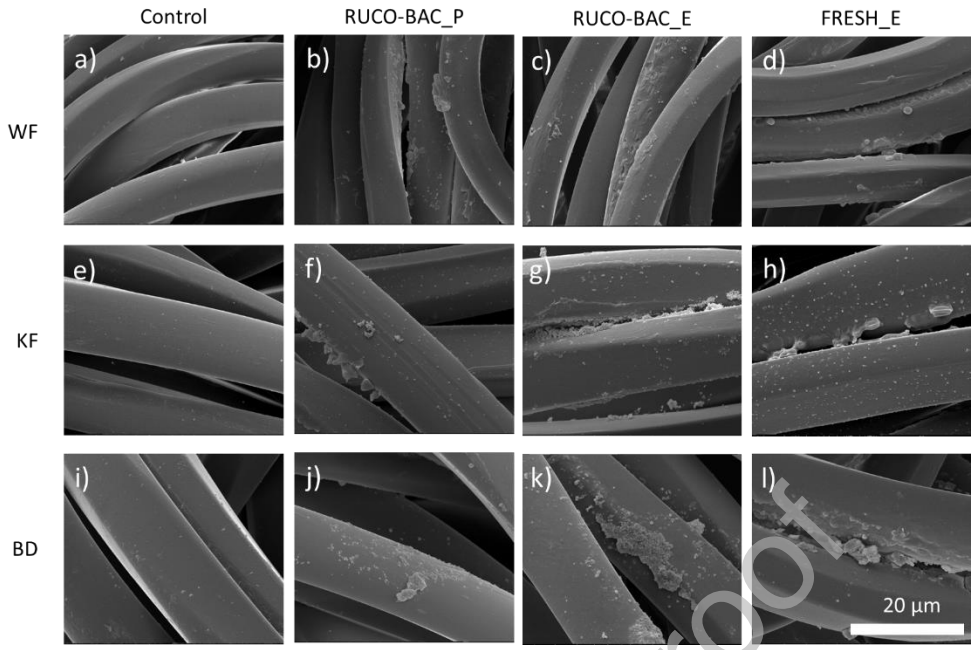


Figure 2. SEM images of a) WF control, b) WF RUCO-BAC_P, c) WF RUCO-BAC_E, d) WF FRESH_E, e) KF control, f) KF RUCO-BAC_P, g) KF RUCO-BAC_E, h) KF FRESH_E, i) BD control, j) BD RUCO-BAC_P, k) BD RUCO-BAC_E, l) BD FRESH_E. Images were collected using a secondary electron detector at a tensile acceleration of 10 kV.

The smooth surface of the control fibers is in accordance with their synthetic composition [31]. Control fibers contain scarcely populated with spots comprising an inferior size to 1 µm may be due to environmental contamination. All functionalized elastic bands exhibit scattered debris-like particles with an uneven size distribution that are not present on the control samples. Thus, these debris-like materials correspond to the antimicrobial agents. There are no clear differences between the types of elastic bands and the agglomeration observed. This indicates that there is a ubiquitous lack of uniformity within finishing processes, compounds, and types of elastic bands. Both processes and products gave rise to samples exhibiting similar surface modification. Nevertheless, FRESH seems to be more evenly distributed throughout the fiber surface. This may be due to a higher chemical/electrostatic compatibility between the PA and EL and FRESH in comparison to RUCO-BAC.

3.2. Water contact angle

The WCA of the elastic bands is displayed in Figure 3. Due to the small diameter and uneven topography of the elastic bands, at least 10 measurements in different sample areas were collected.

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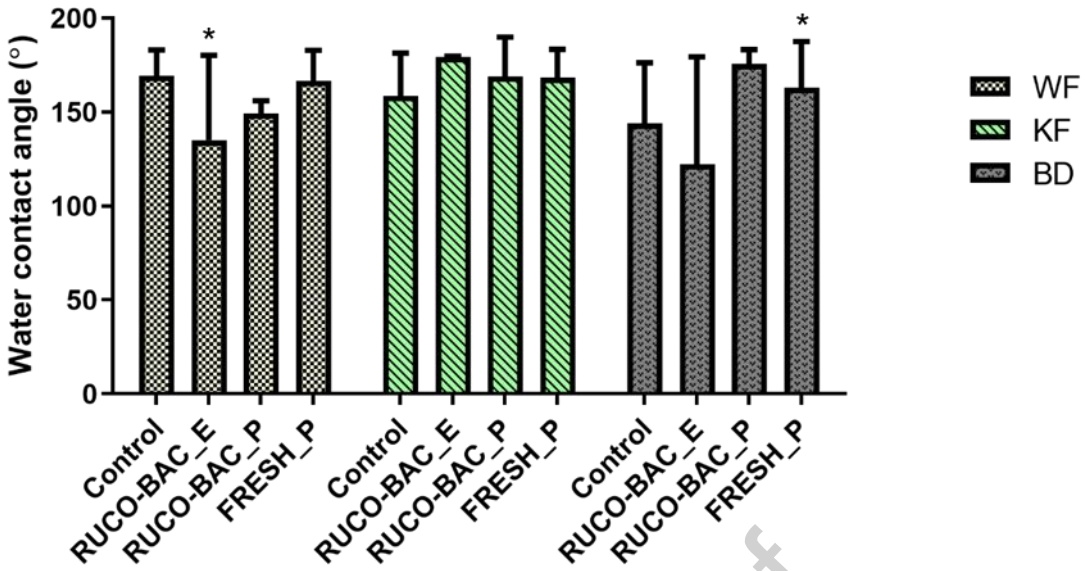


Figure 3. WCA of the elastic bands tested. The * represent the statistical differences observed by one-way ANOVA with Dunnett's multiple comparison (p-value < 0.05), between functionalized samples and the control within each type of elastic band.

WF and KF elastic bands clearly exhibited superhydrophobic water contact angles (> 150°), corresponding to the elastic bands with the highest EL percentage. BD displayed near superhydrophobic nature (approximately 144° ± 32°). PA contains ketone and secondary amines that promptly interact with water through hydrogen bond formation with water molecules, thus PA fibers reported in the literature exhibit WCA of approximately 86°, being characterized as hydrophilic [31-33]. However, EL comprises methylene and aromatic groups, known for conferring higher hydrophobicity, governing the WCA according to their concentration. For instance, PA containing 8% of EL exhibits nearly 115° WCA, while higher WCA are observed for BD with12 % of EL and even higher for WF and KF containing 22 and 38% of EL, respectively [34]. Interestingly, only the exhaustion functionalization clearly impacted the WCA, but solely for WF and KF elastic bands. WF functionalized with RUCO-BAC_E denoted a considerable reduction of its wettability (nearly 1.4-fold), whereas KF with FRESH_E displayed a considerable increase (approximately 1.1-fold). It should be noted that all elastic bands functionalized with FRESH_P reported a superhydrophobic behavior. The distinct chemical composition of the RUCO-BAC and FRESH may be the main factor for these differences.

The washing fastness was solely tested for the padding finishing due to the poor antimicrobial performance of the elastic bands functionalized through exhaustion.

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3.3. Dimensional stability

The percentage of DV after the first and 50 wc was used to determine if the functionalization enhanced or prevented the variation of the elastic band size (Figure 4).

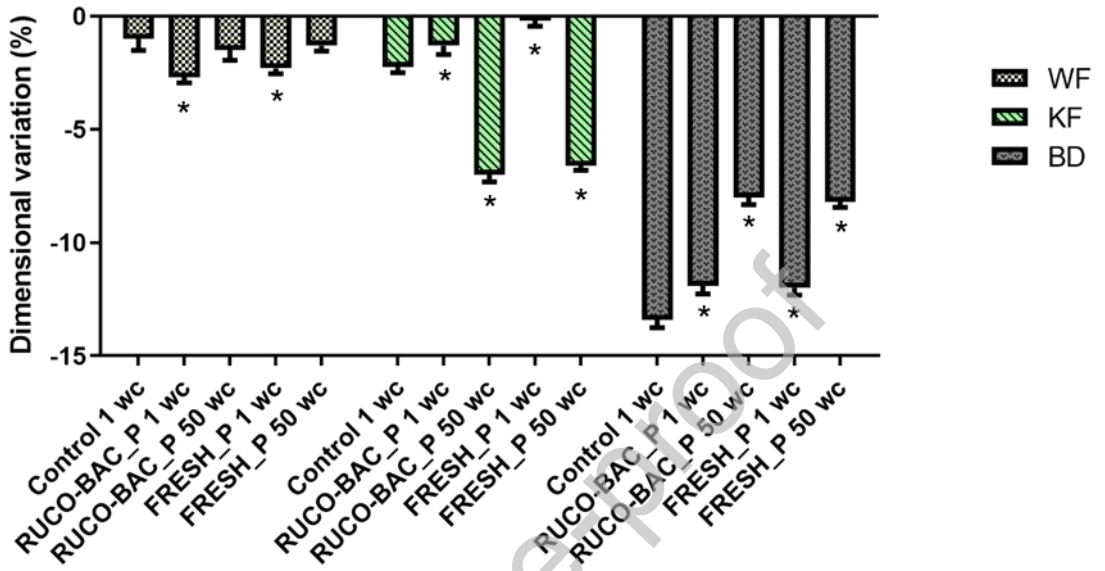


Figure 4. Percentage of DV of the elastic bands functionalized through padding after 1 and 50 wc. The * denote the statistical differences by one-way ANOVA with Dunnett's multiple comparison (p-value < 0.05), between functionalized samples and the control within each type of elastic band.

The dimensional stability (Figure 4) was considerably impacted after 1 and 50 wc, except for WF after 50 wc. WF displayed the slightest DV, and BD showed the highest DV (overall average of -1.7% and -10.7%, respectively). The DV of KF was minor after 1 wc but was expressive after 50 wc. The trend of behavior is distinct for each architecture. In WF, the DV negatively increased after 1 wc, and negatively diminished after 50 wc. Whereas KF displayed the opposite trend, the DV negatively diminished after 1 wc and negatively increased after 50 wc. Finally, BD consistently negatively diminished with increasing wc numbers.

These results underscore the influence of textile architecture as main governing property for the behavior and trend, as EL concentration is higher in KF however its DV is completely distinct from BD [35, 36].

3.4. Mechanical properties

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The mechanical properties of the elastic bands functionalized with the two antimicrobial compounds through padding are shown in Figure 5.

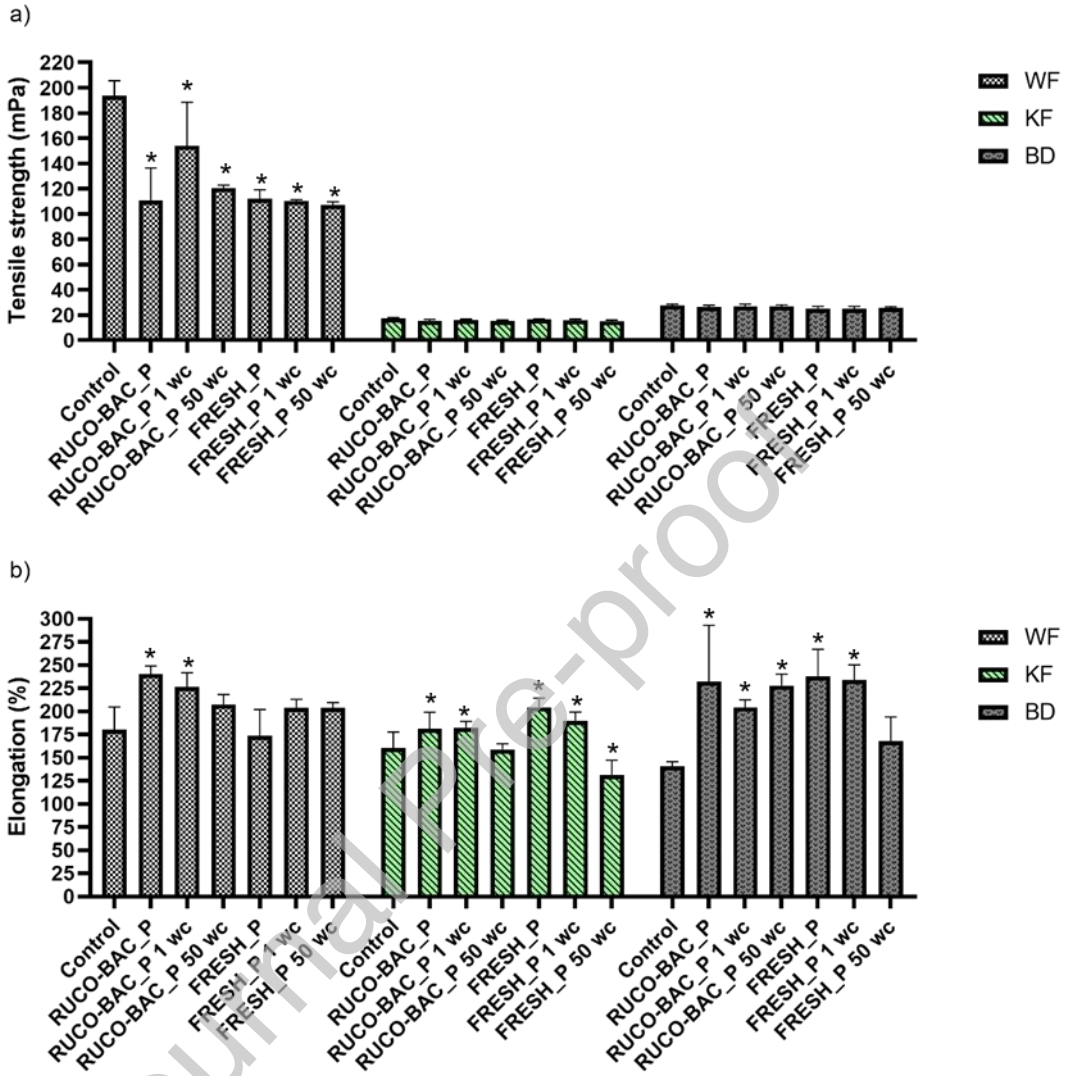


Figure 5. Elastic bands mechanical properties: a) tensile strength and b) elongation percentage. The * represent the statistical differences found by one-way ANOVA with Dunnett's multiple comparison (p-value < 0.05), between functionalized samples and the control within each type of elastic band.

The WF control displayed the highest maximum tensile strength (194±12 mPa), followed by BD (28±1 mPa) and KF (17±1 mPa). The padding using the two antimicrobial finishings displayed obvious reduction of the tensile strength for WF with and without wc (overall nearly 1.6-fold). Interestingly, this was not observed for KF and BD, which maintained their values, even though KF and BD comprise the highest and lowest EL content, respectively. The control group displayed 180%, 160% and 140% of elongation, respectively for WF, KF and BD. These values are

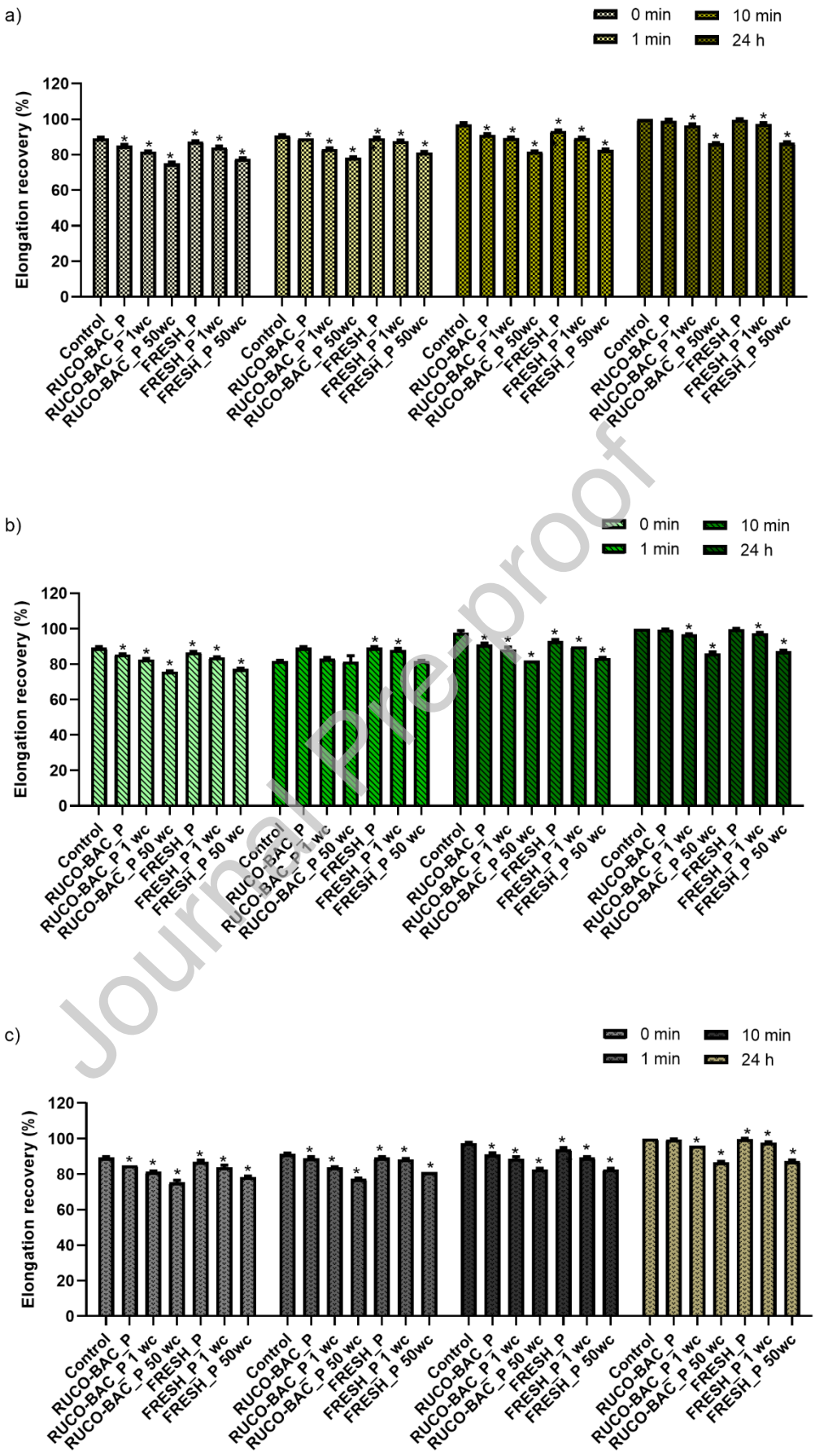
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characterized as medium elongation textiles (low: 20 to 100%, and high: 300 to 800%) [37]. Plain single knitted fabrics commonly exhibit between 150 and 250%, thus KF is within the expected range [38]. After padding with RUCO-BAC, the elongation displayed a relevant increase (1.33-fold), as well as after 1 wc (1.25-fold). However, after 50 wc the elongation is within the range of the control sample. FRESH functionalization did not restrict the elongation. RUCO-BAC and FRESH functionalization increased the elongation of KF, including after 1 wc, in comparison to the control in approximately 1.14-fold and 1.23-fold for RUCO-BAC and FRESH, respectively.

After 50 wc, the elongation of RUCO-BAC functionalized KF was similar to the control; however, KF with FRESH exhibited a relevant decrease (1.22-fold). A reduction in the elongation was only observed in KF functionalized with FRESH after 50 wc. The elongation was clearly higher in the BD functionalized elastic bands (approximately 1.6-fold). Only the BD functionalized with FRESH after 50 wc displayed an elongation similar to the control.

The percentage of ER after different periods of time is shown in Figure 6.

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Figure 6. Percentage of ER immediately after removing the sample from the dynamometer (0 min), after 10 min, 10 min and 24 h of the elastic bands: a) WF, b) KF and c) BD. The * represent the statistical differences found by one-way ANOVA with Dunnett's multiple comparison (p-value < 0.05), between functionalized samples and the control within each type of elastic band at each time point.

The ER (Figure 6) is a key factor for elastic materials, as it partially characterizes the resilience of the elastic band. WF exhibited an obvious decrease in ER, and as expected this was aggravated with increasing number of wc. It was only after 24 h that the functionalized samples exhibited the same elongation recovery as the control. It should be noted that no clear differences were detected between finishing compounds. KF functionalized displayed a similar profile as WF, except after 1 min of recovery where RUCO-BAC_P, FRESH_P and FRESH_P 1 wc displayed a higher recovery in comparison to the control (approximately 1.2-fold). BD elongation recovery was considerably lower for all elastic bands in comparison to the control, except for BD RUCO-BAC_P after 24 h. Table 3 displays the ER linear rate within the first 10 min.

The higher ER rates were observed in the control elastic bands. KF control exhibited the highest recovery rate, which was expected due to its higher EL concentration. Interestingly, all RUCO-BAC_P elastic bands displayed a lower ER rate in comparison to RUCO-BAC_P 1 wc. Overall, WF and BD RUCO-BAC_P, WF and BD RUCO-BAC_P 1 wc, WF and BD RUCO-BAC_P 50wc and WF and BD FRESH_P display a reduction of between 1.1 and 1.3-fold in comparison to the control. However, WF and BD FRESH_P 1 wc and FRESH_P 50 wc display a near 2-fold reduction in the ER rate. This denotes an impact of the FRESH functionalization.

A higher reduction was observed in KF elastic bands, ranging between 2 to nearly 3-fold for functionalized elastic bands after 50 wc.

Table 3. Elastic band linear elongation recovery rate between 0 and 10 min.

	WF	KF	BD
	(% min^{-1})		
Control	0.76 ± 0.45	1.20 ± 0.23	0.74 ± 0.04
RUCO-BAC_P	0.45 ± 0.10	0.42 ± 0.10	0.45 ± 0.10
RUCO-BAC_P 1 wc	0.74 ± 0.04	0.58 ± 0.05	0.66 ± 0.06
RUCO-BAC_P 50 wc	0.55 ± 0.08	0.41 ± 0.17	0.68 ± 0.06
FRESH_P	0.55 ± 0.04	0.54 ± 0.06	0.63 ± 0.06
FRESH_P 1 wc	0.40 ± 0.10	0.47 ± 0.10	0.39 ± 0.12

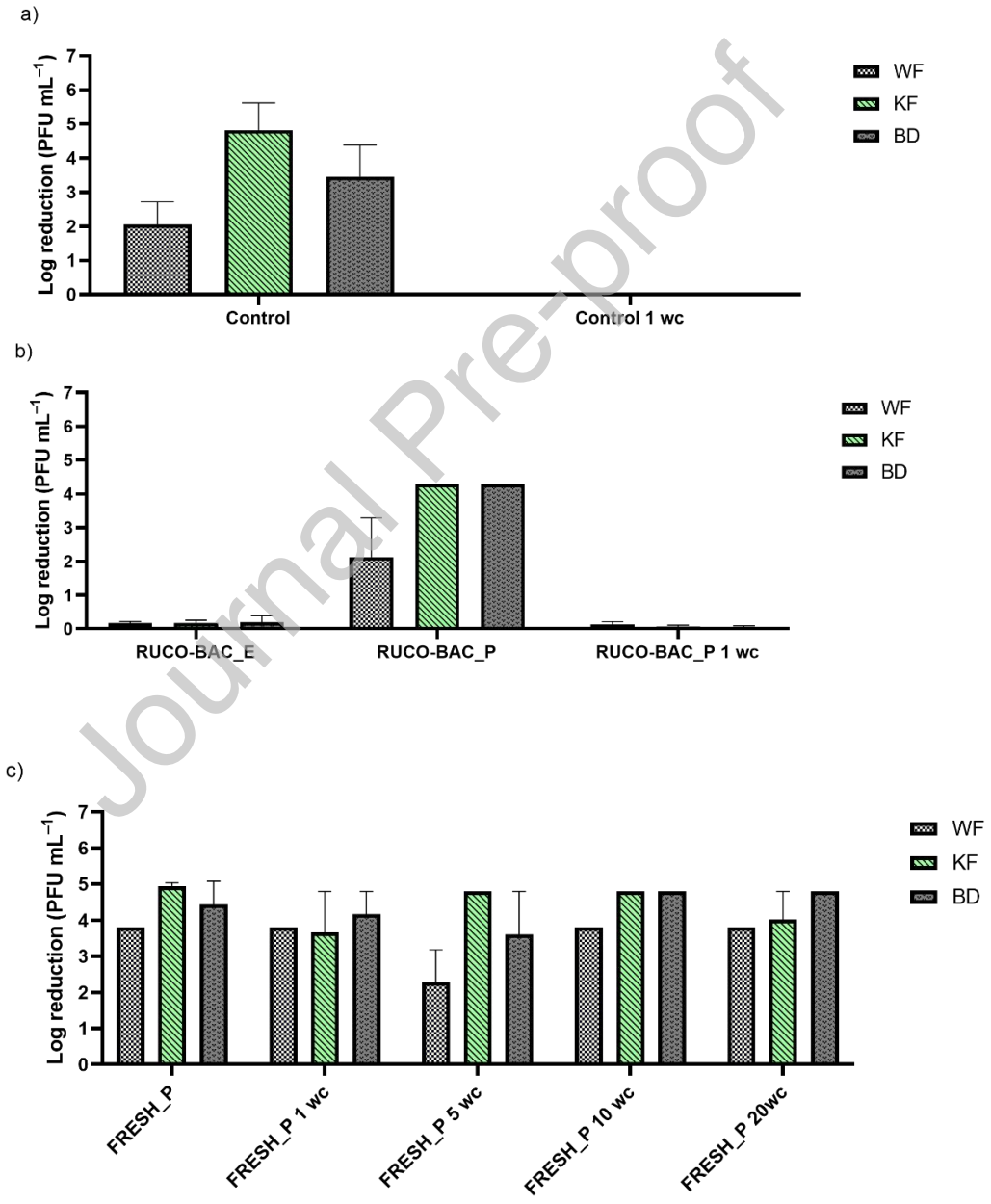
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FRESH_P 50 wc	0.38 ± 0.08	0.44 ± 0.10	0.34 ± 0.06

0.Globally, it is clear the impact of wc for ER that is independent of the functional finishing and elastic band architecture.

3.5. Antimicrobial activity

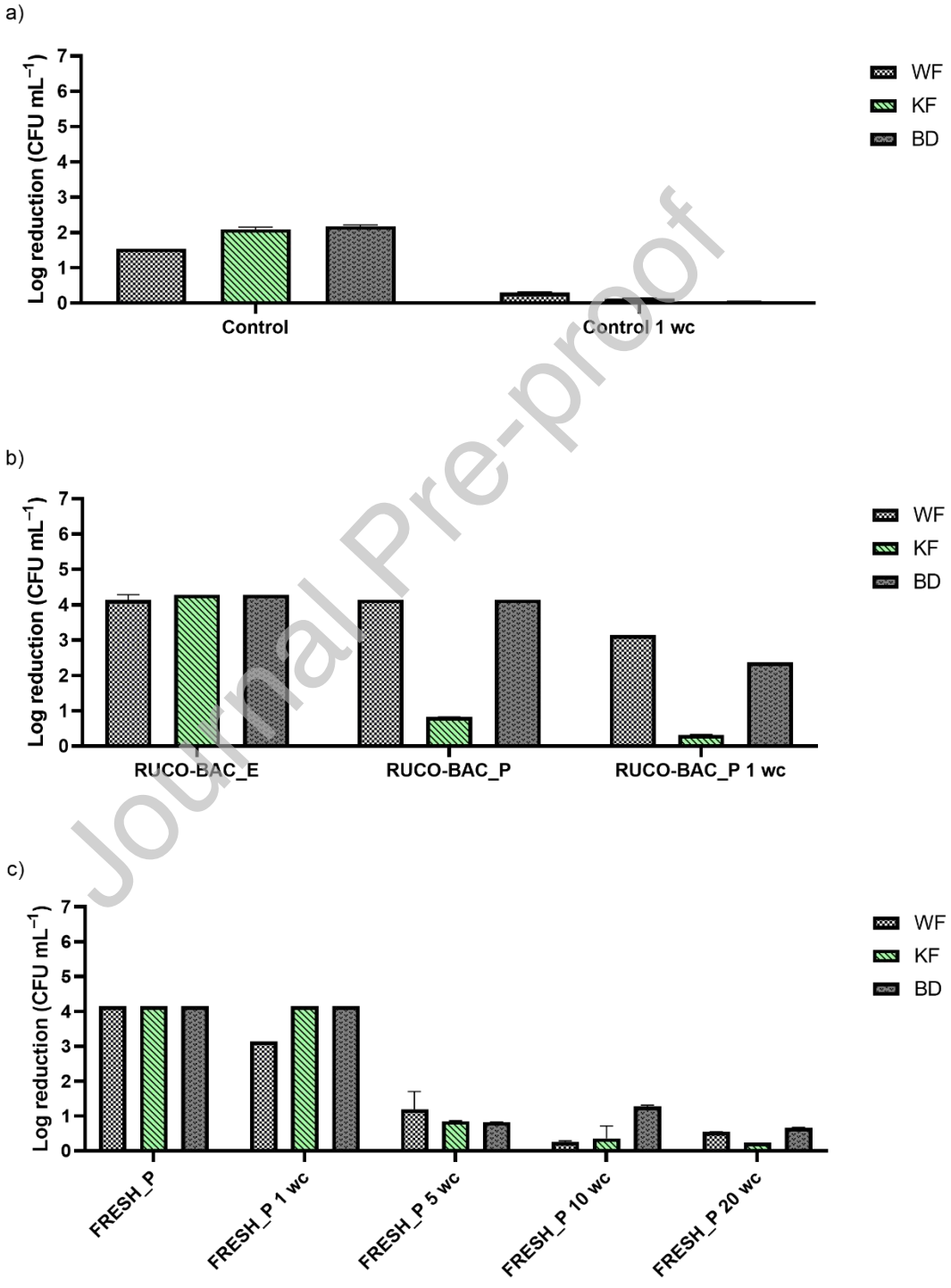
The antiviral activity of the elastic bands is displayed in Figure 7.



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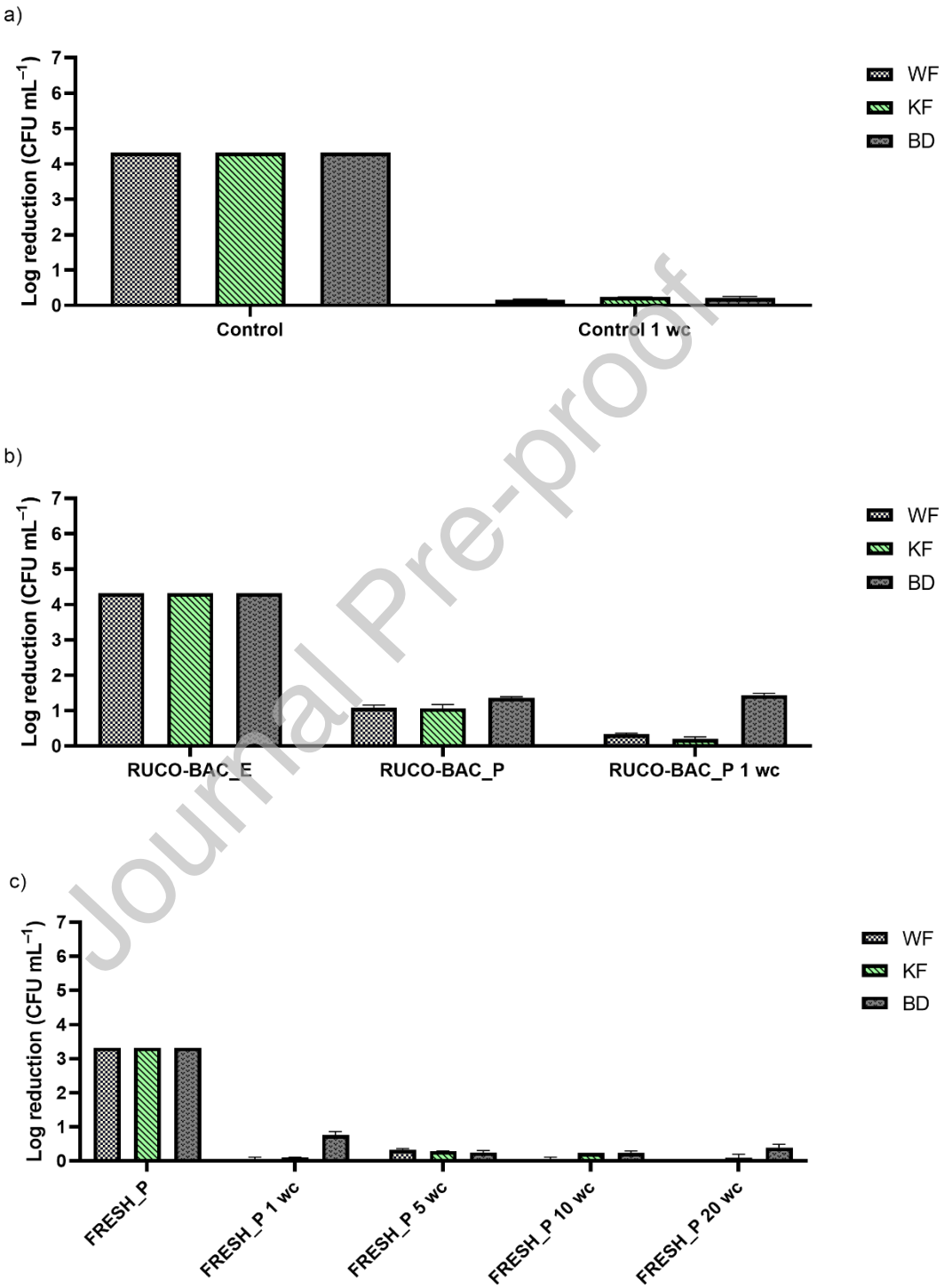
Figure 7. MS2 bacteriophage antiviral activity of the elastic bands: a) control elastic band without functionalization, pristine (as received from the manufacturer) and after 1 wc, b) functionalization using RUCO_BAC, including 1 wc after padding and c) FRESH functionalization performance after 1 to 20 wc.

The antibacterial performance of the elastic bands is exhibited in Figures 8 and 9.



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Figure 8. Antibacterial activity against *S. aureus* of the elastic bands: a) control elastic band without functionalization pristine (as received from the manufacturer) and after 1 wc, b) RUCO-BAC functionalizations and 1 wc after padding and c) FRESH finishing performance after 1 to 20 wc.



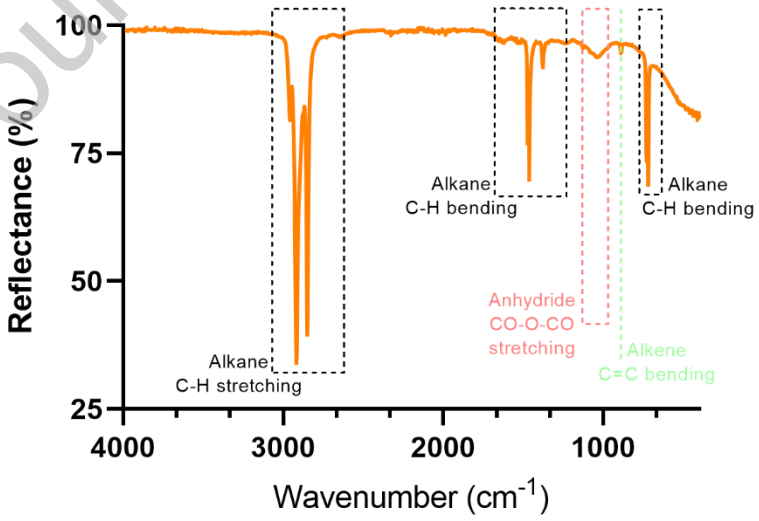
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Figure 9. *P. aeruginosa* antibacterial activity of the elastic bands: a) control elastic band without functionalization, pristine (as received from the manufacturer) and after 1 wc b) RUCO-BAC finishings and 1 wc after padding and c) FRESH functionalization performance after 1 to 20 wc.

Antimicrobial evaluation highlighted the relevant antiviral and antibacterial activity of the control samples. MS2 viable concentration was reduced nearly 2-log, 5-log and 3-log when in contact with WF, KF, and BD control samples. The reduction was milder for *S. aureus*, nearly 2-log reduction for all elastic bands. *P. aeruginosa* reduction was 4-log for all samples. Interestingly, this antimicrobial activity was completely suppressed after 1 wc. During the textile production paraffin wax is commonly used to reduce friction between fibers during spinning, weaving and knitting, facilitating manufacturing process [39]. Paraffin is composed of linear chains of alkanes in between 80 to 90% of its constitution [40]. Paraffin used for textile processes may possess additional substances and additives tailored to the targeted fiber taxonomies (such as fiber constitution and/or structural attributes such as linear density) [41].

A notorious example is the commonly named "waxed rolls" used to paraffin yarns during knitting and weaving. These paraffin rolls may even contain emulsifiers in their composition to facilitate the solubility of paraffin once in contact with water, for its prompt elimination from the textile. These compounds may also possess antimicrobial properties to prevent microbial growth during storage [42].

A paraffin roll commonly used in the textile industry (MEZGER inc.) was analyzed through FTIR-ATR (Figure 10).



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Figure 10. Paraffin roll FTIR-ATR spectrum. Alkane characteristic functional groups are encased by black dashed boxes. Possible anhydride and alkene vibration bands are highlighted by red and green dashes based on the information collected in [43].

The spectrum highlights the presence of the typical vibration bands of alkanes, namely: C-H stretching (2850, 2916 and 2960 cm^{-1}), C-H bending (1466 and 1376 cm^{-1}) and long chain C-H bending (716 cm^{-1}). However, there is the presence of hypothetical anhydride CO-O-CO stretching (1040 cm^{-1}) and a possible alkene (C=C) bending (890 cm^{-1}), both not attributable to paraffin [43]. This may denote the presence of maleic anhydride or acetic anhydride, commonly used in the textile industry [40, 44]. Thus, corroborating the presence of additional components in paraffin and, hence, explaining the absence of activity after 1 wc. The RUCO-BAC did not exhibit any antiviral activity against MS2, encapsulated bacteriophage, when applied through exhaustion. All elastic bands functionalized through padding displayed an expressive virucidal activity against MS2. However, after 1 wc, this activity was depleted.

RUCO-BAC functionalization through exhaustion exhibited a relevant antibacterial activity against *S. aureus* and *P. aeruginosa*. Interestingly, through padding, RUCO-BAC did not demonstrate any activity against *P. aeruginosa*, as well as KF against *S. aureus*. Furthermore, its activity was diminished after just 1 wc. Therefore, the performed characterization was more important for FRESH, due to RUCO-BAC inefficiency against MS2. Furthermore, padding represents an overall more cost-effective method and generates less wastewater.

Water is a key resource for the environmental viability of the textile industry. The functionalization of the elastic bands with FRESH exhibited a robust antiviral, even after 20 wc, displaying a moderate to strong disinfection. Its performance against *S. aureus* was of moderate disinfection and was maintained after 1 wc. However, after 5 wc the antibacterial activity dropped to a weak decontamination. All elastic bands functionalized with FRESH displayed a poorer performance against *P. aeruginosa* (weak disinfection). Furthermore, it exhibited no antibacterial activity after 1 wc. Consequently, the milder activity of FRESH towards this eclectic microorganism was completely depleted after 1 wc, indicating that probably the FRESH concentration in the elastic bands is diminished during each wc. Nevertheless, its strong efficacy is maintained against *S. aureus* and MS2 after 1 and 20 wc, respectively.

These insights allow the elaboration of a hypothetical FRESH antimicrobial modus operandi. Considering that FRESH comprises some washing fastness, it will not be readily released into the PBS containing the different inocula. If so, its antimicrobial activity will undergo through the direct contact between the FRESH coating and the microbial surface. MS2 bacteriophage is an

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encapsulated virus, possessing an icosahedral protein capsid that surrounds its genome composed of positive-sense single-stranded (+ss) RNA [45, 46].

In addition to the coating, proteins MS2 possess a single maturation protein. Maturation protein plays a pivotal role in host infection process, furthermore it ensures the correct encasing of the genomic material and capsid assembly during virion replication [47, 48]. Thus, MS2 surface is mainly comprised of proteins. *S. aureus* has a thick peptidoglycan layer in its cell wall, which is a defining feature of Gram positive bacteria [49]. This cell wall is heavily populated of teichoic acids and encompasses surface proteins such as: transporters, adhesins, proteins involved in cell signaling, enzymes involved in nutrient metabolism, and protein A, a unique protein form this bacterium [49-51]. *P. aeruginosa*, as Gram negative bacterium, the first surface that will interact with the surface of the substrate is the outer layer, mainly composed of lipopolysaccharides [52, 53]. It also contains phospholipids and proteins, such as Gram positive bacteria, namely: porins, transporters, adhesins, among others [54]. Furthermore, this bacterium contains intramembrane proteins that are not readily available to interact with the antimicrobial finishing. Thus, it can be hypothesized that the concentration of available surface proteins is higher in the MS2, followed by *S. aureus* and finally by *P. aeruginosa*.

This may be correlated with the antimicrobial efficacy of FRESH. Based on this hypothesis, if FRESH main activity is against proteins, amino acid hydrophobicity level can have some interference during the interaction with FRESH. Three icosahedral faces of the MS2 capsid were colored according to their hydrophobicity according to the Kyte-Doolittle hydrophobicity scale (Figure 11). The most hydrophobic amino acids residues (containing a hydrophobicity value higher than 2) were colored in black. Hydrophobic amino acid residues (comprising a hydrophobicity value between less than 2 and higher than 0) were colored in dark grey. Hydrophilic amino acids residues (hydrophobicity level between 0 and -2) and highly hydrophilic amino acids (hydrophobic value lower than -2) were colored in light blue and red, respectively.

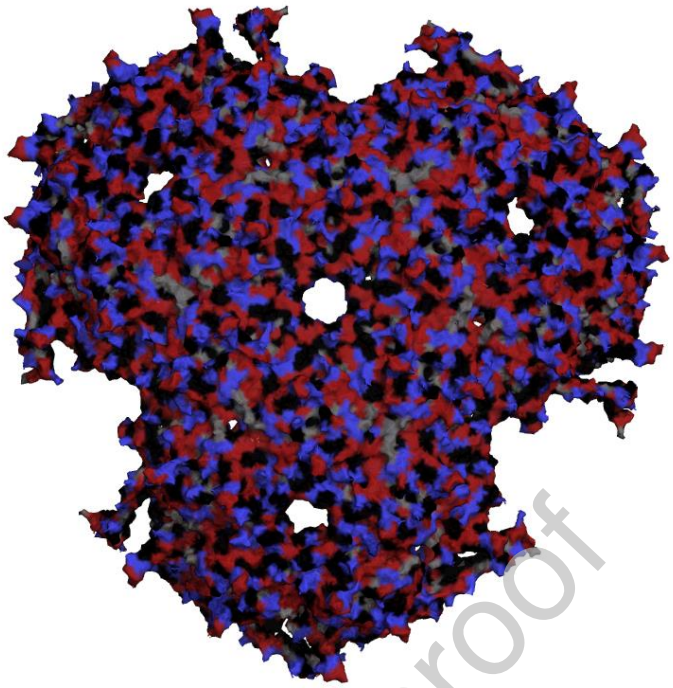


Figure 11. Image was obtained using Protein Data Bank file "1GAV" in PyMOL (DeLano Scientific).

Although the presence of homogenous distribution hydrophobic is observable, the presence of hydrophilic amino acids apparently governs the surface of MS2 capsid. Due to the small size of MS2 virions (approximately 27 nm), it possesses a high surface to interact with FRESH present in the elastic bands [55].

This may be correlated with high anti-viral efficacy of FRESH at lower concentrations after 50 wc. One of the proposed actions of quaternary ammonium silanes is the denaturation of proteins. Due to the protein based capsid of MS2, this may be the primary anti-virucidal activity unfolding in this case.

Interestingly, Gram positive bacteria surface is considered more hydrophobic. Thus, *S. aureus* may be attracted to the superhydrophobic surface of the elastic bands. Whereas Gram negative bacteria tend to have a more hydrophilic surface. While the lipid A region is hydrophobic, the presence of the O antigen, with its carbohydrate components, imparts hydrophilic properties to the overall structure of LPS. In summary, FRESH may be primarily denaturing the proteins of the microorganisms, thus MS2 and *S. aureus* are more sensitive to this agent. Furthermore, *P. aeruginosa* may be prone to be repelled by the superhydrophobic surface of the elastic bands, further impairing FRESH efficacy.

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4. Conclusions

The characterization of antimicrobial finishings available in the literature is extensive for a wide range of fibers and textile architectures, encompassing non-woven, knitted and woven textiles. However, it is extremely difficult to find references dedicated to study the impact of antimicrobial finishings in elastic bands. Thus, it is unclear their efficacy, impact on their mechanical properties, and washing fastness behavior.

This work was focused on the unraveling these parameters, thus, three different elastic bands were functionalized with two different commercial antimicrobial finishings. The antimicrobial finishings not only prevent the potential spreading of pathogenic microorganisms, but also may enhance textile longevity, thus enhancing their sustainability. However, their wide range efficacy must not markedly impair the mechanical properties and must display satisfactory washing fastness.

Subsquently to functionalization, increasing wc impacted the elastic bands differently in accordance with their architecture. The WF exhibited the best performance in preserving the dimensional variation, however its tensile strength was significantly diminished, whereas for KF and BD was maintained. The elongation was, in terms of trend, more heavily influenced in the BD, in particular functionalized RUCO-BAC, even after 50 wc, in opposition to all other samples. Interestingly, the ER displays similar trends for all tested samples. Thus, the elastic band architecture and type of functionalization is not pivotal in setting the trends of mechanical behavior, except for particular described analysis.

To provide an overview of antimicrobial activity, two different bacteria, one Gram positive and one Gram negative, and a bacteriophage were used. The two commercial antimicrobial finishings studied (RUCO-BAC and FRESH) did not impact equally the three distinct types of elastic bands (WF, KF, BD). Both antimicrobial finishing agents provided antimicrobial activity to the elastic bands. However, their washing fastness may be considered poor. The renowned exception are the elastic bands functionalized through padding using FRESH, that exhibited antiviral activity after 20 wc. FRESH antimicrobial activity was hypothesized to be focused on the denaturation of surface viral and bacterial proteins.

Interestingly, the antimicrobial evaluation led to the finding of an expressive antimicrobial and antiviral activity of the pristine elastic bands. It was hypothesized that this activity is due to the presence of antimicrobial components in lubricants and softening agents commonly used in the elastic bands production. More importantly, this activity is completely eliminated after a single wc, underscoring the need for antimicrobial finishings.

As observed, it is possible to functionalize elastic bands commercially available antimicrobial finishing, using standardized equipment form the textile industry, without hindering their main purpose: elasticity. Generally, for the tested microorganisms the washing fastness was unsatisfactory, which may also be correlated to their high concentration of EL. Their loss of activity may be correlated to the ineffective washing fastness of the antimicrobial finishings on elastic bands. Thus, once these finishing components and methodologies are applied in textiles containing indwelled elastic bands, there is a potential of a high and premature release of the finishings. Considering that they are antimicrobial finishing, they may have a considerable negative impact on the environment or even in the wastewater treatment plants microflora. Therefore, the optimization of the application of antimicrobial, and other finishings on textiles comprise high concentrations of EL should be undertaken. This need is further exacerbated by the near absence of references focused on elastic band characterization.

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Writing – review and editing. **Jorge Padrão:** Conceptualization, Methodology, Supervision, Project administration, Visualization, Writing – original draft, Writing – review and editing

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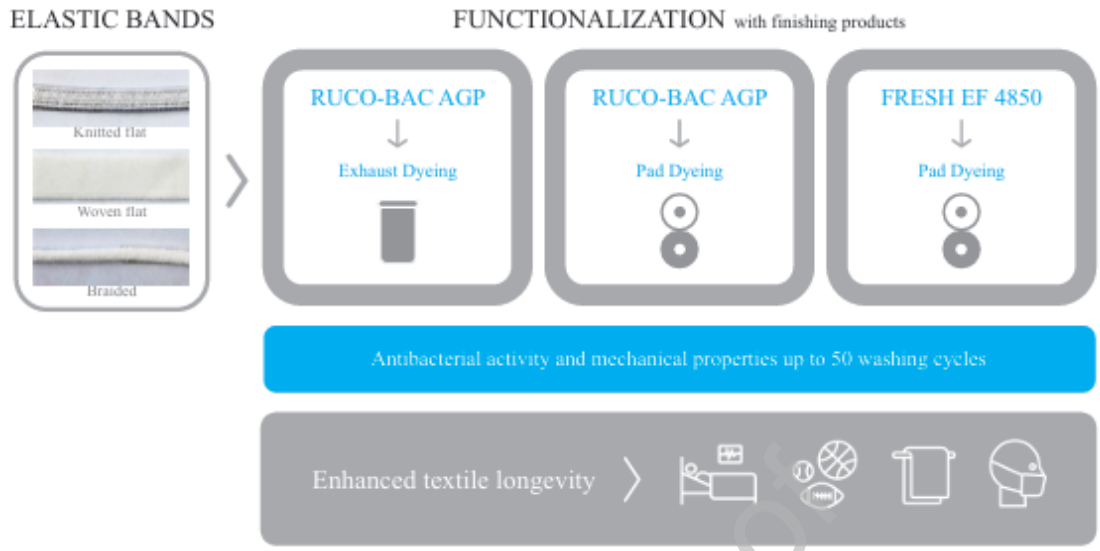
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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