

Article

Aqueous Polyhydroxyalkanoate Solution-Based Knife Coatings: An Alternative Approach to the Production of Coated Cotton Fabrics

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Abstract

Footwear is traditionally manufactured using non-biodegradable polymers and leather, raising well-documented environmental and health concerns related to their production and disposal. This study explores polyhydroxyalkanoates (PHAs) as sustainable alternatives for bio-based footwear components. A stable aqueous suspension of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) was successfully formulated and applied to cotton fabrics via knife-coating. Various formulations, with and without additives and employing natural or synthetic thickeners, were evaluated in terms of surface morphology, wettability, permeability, and durability. The 10% PHBHHx formulation provided the best balance between material efficiency, coating uniformity, and surface performance. Additives and thermal treatment both influenced wettability, reducing contact angles and enhancing water vapor permeability. Notably, coatings with additives and hot pressing exhibited the highest permeability ($68.0 \pm 3.1 \text{ L/m}^2/\text{s}$; $651.0 \pm 5.4 \text{ g/m}^2/24 \text{ h}$), while additive-free, non-pressed coatings showed significantly lower values ($19.5 \pm 4.4 \text{ L/m}^2/\text{s}$; $245.6 \pm 66.2 \text{ g/m}^2/24 \text{ h}$), likely due to excessive compaction. Abrasion resistance remained excellent across all samples, especially with thermal treatment, withstanding 51,200 cycles. Washing resistance results revealed a synergistic effect between additives and heat, promoting long-term hydrophobicity and coating adhesion. Overall, PHBHHx coatings demonstrated potential to enhance water resistance while maintaining breathability, representing a sustainable and effective solution for functional and technical footwear applications.

Keywords: footwear; poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx); biopolymers; cotton fabric; rheology modifier



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1. Introduction

Growing awareness of the environmental impacts associated with the excessive use of synthetic materials and the accumulation of non-biodegradable waste has intensified global interest in more sustainable alternatives. This shift aligns with the principles of the circular economy, which emphasize recycling, resource efficiency, and reduced dependence on virgin raw materials [1]. Despite growing environmental concerns, the footwear industry continues to rely heavily on petroleum-based synthetics and animal-derived leather [2]. Consumption patterns are shaped by rising disposable incomes, changing fashion trends, an expanding working-class population, and the rapid growth of e-commerce platforms.

According to the European Environment Agency (EEA), average per capita footwear consumption in the EU rose from approximately 3.2 kg in 2019 to 4.4 kg in 2022, reflecting a significant 38% increase [3]. Footwear is commonly manufactured using a variety of materials, including leather, canvas, polyurethane (PU), polyvinyl chloride (PVC), vulcanized rubber, and ethylene-vinyl acetate (EVA), along with accessories like shoelaces and eyelets. These components collectively contribute to the industry's substantial environmental footprint, not only because of energy-intensive production methods but also, in the case of leather, due to hazardous chemical treatments necessary to make it usable [4,5]. Leather, traditionally sourced as a by-product of the livestock industry, is prized for its exceptional properties, including durability, mechanical strength, water vapor permeability, abrasion resistance, biodegradability, and biocompatibility [6,7]. However, achieving specific performance enhancements, such as increased water resistance or breathability, requires intensive chemical processing. Processes like tanning and surface finishing introduce considerable environmental and human health hazards [8]. Chromium salts are central to tanning, with chromium (III) employed in approximately 90% of global operations [9]. During processing, a fraction of chromium remains unfixed and is discharged into wastewater, where it can oxidize into chromium (VI), a recognized carcinogen and persistent environmental pollutant [10]. Similarly, polyvinyl chloride (PVC), a widely used synthetic leather substitute, presents severe ecological and health challenges throughout its lifecycle, from production to disposal [11]. PVC releases hazardous compounds including dioxins and phthalates. Dioxins are persistent, bioaccumulative endocrine-disrupting chemicals (EDCs) with serious implications for both human health and ecosystems. Phthalates, frequently added in high concentrations as plasticizers to enhance flexibility, are also known EDCs, raising significant public health concerns [12,13]. Consequently, governments and manufacturers worldwide are actively pursuing safer and more sustainable alternatives to these materials.

In response, increasing scrutiny of materials derived from both animal and synthetic sources has driven the development of plant-based or vegan leathers made from renewable feedstocks such as pineapple leaf fibres [14], sawdust [6], and mushroom-derived chitin [15]. Additionally, composites incorporating agro-biomass residues as bio-fillers, such as bacterial cellulose and tree leaves (e.g., maple leaves) have also emerged as promising alternatives. These bio-fillers are often combined with polymer matrices such as polycaprolactone (PCL), polylactic acid (PLA), and polyvinyl alcohol (PVA), which have been widely used in the development of sustainable alternatives to leather materials [16]. Other footwear components, such as insoles and toe-puffs have also been developed using clothes and agro-industrial wastes [6,17]. Biodegradable materials have gained significant attention as viable solutions. These materials not only support environmental sustainability but also help educate producers and consumers about responsible consumption and end-of-life disposal [18]. Among the most promising biodegradable materials are polyhydroxyalkanoates (PHAs), a class of thermoplastic polyester produced via microbial fermentation. PHAs naturally degrade across diverse environmental conditions without leaving persistent residues [19,20]. Within the PHA family, the copolymer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) has gained considerable attention for its balanced flexibility, mechanical strength, moisture resistance, and biodegradability, offering distinct advantages over other polymers used in footwear development, such as PLA, particularly for certain components [21]. Produced from renewable feedstocks via microbial fermentation, PHBHHx offers a substantially reduced environmental footprint compared to conventional petroleum-based polymers [22]. Unlike traditional synthetic coatings, PHBHHx is fully biodegradable under appropriate conditions, effectively addressing critical issues related to plastic waste and microplastic pollution [23]. Despite

its potential, the practical application of PHBHHx as a coating on cotton fabrics used in footwear components remains insufficiently explored, particularly regarding adhesion to textile substrates, water vapor permeability, abrasion resistance, and durability under repeated mechanical stress and laundering.

This study aims to develop a PHBHHx coating applied via the controlled knife coating technique onto cotton fabric and systematically evaluate its potential as a sustainable, high-performance alternative for footwear component applications. To the best of our knowledge, this is the first study to explore PHBHHx coatings for textile-based footwear components, including formulations with and without additives, representing a novel approach in the search for eco-friendly and functional materials. The PHBHHx formulation was precisely deposited using the knife coating method to ensure uniformity and optimal film formation. The coated textiles were subjected to targeted evaluations, including breathability, surface wettability (contact angle measurements), abrasion resistance, and wash durability tests. This comprehensive investigation critically evaluates whether PHBHHx coatings can meet the stringent environmental and functional requirements of the footwear industry. The findings provide valuable insights into the novel potential of PHBHHx, with and without additives, as an eco-friendly material that maintains high performance, highlighting a promising pathway for advancing sustainable footwear manufacturing technologies.

2. Materials and Methods

2.1. Materials and Reagents

A woven fabric composed of 99% cotton and 1% elastane (CO, 369 g/m²) was kindly provided by Riopelle (V.N. Famalicão, Portugal). PHBHHx powder was purchased from Bluepha (Beijing, China) and had a molecular weight of 291,000 Da with a polydispersity index of 4.51. The particle size of the PHBHHx powder was characterized by a distribution with particles measuring ≤ 60 μm . A nonionic surfactant, Tween 20 was kindly provided by Croda Iberica SAU (Barcelona, Spain). DISPERBYK-190, a VOC-free and solvent-free wetting and dispersing additive was acquired from BYK (Wesel, Germany). Xanthan gum, a natural thickener from NatureFoods, and Tubicoat Verdicker LP, a synthetic thickener, kindly supplied by CHT (Tübingen, Germany) were also used. A commercially available household detergent was purchased from a local supermarket and used to perform washing tests on the coated samples.

2.2. Preparation of PHBHHx-Based Coating Formulations

The coating formulations were prepared by dispersing varying concentrations of polymer (PHBHHx) 5%–20% *w/v* in distilled water under continuous stirring for 60 min. To enhance polymer dispersion, a dispersant Disperbyk-190 (BYK, Wesel, Germany) and a surfactant, Tween 20 (Croda International Plc, Snaith, East Yorkshire, UK) were added at concentrations of 0.05%–3% and 0.05%–3% *w/v*, respectively. The mixtures were then sonicated using a QSonica Q700 (QSonica, Newtown, CT, USA) at 65% amplitude for 10 min to ensure homogeneity. Subsequently, the thickeners Xanthan Gum (Naturefoods, Lisboa, Portugal) and Tubicoat Verdicker LP (CHT Group, Tübingen, Germany) were added dropwise under continuous mechanical agitation for an additional 45 min to ensure uniform thickening. The concentration of thickeners in the various coating formulations was adjusted between 0.5% and 2% *w/v* to achieve the desired viscosity for effective application. Viscosity measurements were carried out using a Brookfield DVE™ viscometer (AMETEK Brookfield, Middleboro, MA, USA). An appropriate spindle and rotational speed settings were selected to maintain torque values within the instrument's recommended operating range, thereby ensuring accurate, consistent, and reliable viscosity measurements.

2.3. Application of PHBHHx-Based Coatings on Cotton Fabrics

Cotton fabric samples (30 cm × 25 cm) were coated using a laboratory-scale knife-coating machine (Mathis LABDRYER, Oberhasli, Switzerland). The fabric was first secured and tensioned on a metallic frame integrated into the equipment. The optimized coating formulation was applied in three successive layers: the first layer was applied with a nominal thickness of 0.0 mm (serving as a base or primer), followed by two additional layers, each with a thickness of 0.2 mm. After coating, the samples were oven-dried and simultaneously cured at 170 °C for 10 min under air circulation at 1200 rpm. To further enhance the adhesion of the coating to the textile substrate, the coated fabric underwent a thermofixation step at 180 °C for 15 s under pressure of 4 bar.

2.4. Characterization

2.4.1. Surface Analysis

Surface inspection was performed using a Leica M716 stereomicroscope (Leica Microsystems, Wetzlar, Germany), with adjustable incident illumination and a fixed magnification of 12.5×. Samples were placed on the instrument's base and systematically examined to assess surface features and detect potential defects.

2.4.2. Thickness and Grammage

The thickness of the fabrics, both before and after coating, was measured using a thickness gauge (SCHRÖDER Rainbow, Weinheim, Germany). The fabrics were placed between two plates or sensors, and the thickness was displayed digitally to ensure greater precision. The grammage was determined following ISO 3801: 1977—Textiles—Determination of Mass per Unit Length or Mass per Unit Area.

2.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

Spectra were acquired using a spectrum One spectrophotometer (PerkinElmer, Rodgau, Germany) equipped with an attenuated total reflectance (ATR) accessory. FTIR analysis was performed over the spectral range of 4000–650 cm^{−1}, with a spectral resolution of 8 cm^{−1} and an average of 8 scans per measurement, recording transmittance values at each point. ATR-FTIR spectra were collected in triplicate.

2.4.4. Wettability

Water contact angle measurements were conducted in an optical tensiometer Theta Flex (Biolin scientific, Gothenburg, Sweden) connected to a video-based drop shape analyser OneAttension software (version 1.2), via the sessile drop measuring method, using droplets of 3 µL of H₂O. Ten measurements were performed per type of sample. Static angles were registered immediately after the stable drop contacted with the surface.

2.4.5. Permeabilities

Air and water vapor permeability tests were performed in accordance with ISO 9237:1997 and BS 7209:1990 standards, respectively. Air permeability was measured using a Textest FX 3300 device under an applied air pressure of 200 Pa, a value commonly used for industrial fabrics applications. For each fabric, three samples were tested, with measurements taken at nine equidistant points (20 cm² each) distributed transversely across the fabric surface.

On the water vapor permeability (WVP) assessment, a water vapour permeability tester SDLA ATLAS M261 was used. The samples were placed over cylindrical cups containing 46 mL of deionized water (dH₂O) for 16 hours, with the coated side of the fabric-oriented outward, representing the exterior side of the clothing. Water evaporation through the textile substrates was evaluated by weighing the test cups before and after the exposure period. Experiments were conducted at room temperature (20–24 °C) and 50% relative

humidity. An open cup covered with a reference substrate served as the control. All measurements were performed in triplicate. The water vapor transmission rate (WVTR) and the water vapor permeability index (I) were calculated using the following equations:

$$\text{WVTR} = 24\Delta W / A\Delta t \quad (1)$$

$$I = \text{WVPs} / \text{WVPr} \times 100 \quad (2)$$

where ΔW is the difference in the water weight (g) before and after the 16 h test, A is the inner area of the cup (mm), Δt is the exposure time (h), WVPs is the water vapor permeability of the samples and WVPr is the water vapor permeability of reference.

2.4.6. Abrasion of Fabrics

Four specimens (125 × 125 mm) were randomly cut from different areas of each fabric sample. The specimens were mounted on a Martindale Abrasion Tester (James Heal, Halifax, UK; Model NU 864) following the ISO 5470-2 standard, with a load of 12 kPa applied to each sample. Each specimen was subjected to 51,200 abrasion cycles and evaluated for degradation using a scale from 0 to 5, where 0 indicates no visible damage and 5 signifies complete exposure of the base textile substrate. Wool fabric was used as the abrasive material in these tests.

2.4.7. Resistance to Washing

The tests were conducted using a domestic washing machine. Fabric samples were washed in a solution containing 1 g/L of commercial detergent at 40 °C for 45 min. Each sample underwent up to five washing cycles. After the first and fifth, the samples were dried at 100 °C for 5 min prior to further analysis.

3. Results and Discussion

3.1. Development of Aqueous PHBHHx Knife Coatings

3.1.1. Preparation and Application of Stable Aqueous PHBHHx Suspensions Using Knife Coating

The knife coating method was selected for the deposition of PHBHHx coatings onto cotton fabrics due to its ability to form uniform layers, allow precise control over coating thickness, and ensure compatibility with industrial-scale processing. The primary aim of this study was to develop such coatings through an environmentally sustainable approach. In alignment with the sustainability goals of the associated European research project, particular emphasis was placed on formulating a stable aqueous PHBHHx suspension, thereby avoiding the use of harmful organic solvents.

PHBHHx, used as the dispersed phase, consists of solid polymeric particles with sizes up to approximately 60 µm, while distilled water serves as the continuous phase. According to dispersion classification, this system qualifies as a suspension [24]. However, the intrinsic hydrophobicity of PHBHHx posed a considerable challenge to achieve a stable suspension in water. To address this, a systematic optimization of formulation parameters was carried out. Key factors investigated included particle size distribution (granulometry), polymer concentration, and the type and amount of surfactants and dispersing agents. Additionally, process conditions such as stirring speed and sonication time were optimized to enhance suspension homogeneity and stability.

To assess the influence of polymer concentration on the coating properties, aqueous suspensions containing 5%, 10%, 15%, and 20% *w/v* of PHBHHx were prepared. All formulations exhibited good physical stability and were deemed suitable for coating applications. Tween 20 and Disperbyk 190 were identified as the most effective additives

for promoting uniform dispersion of polymeric particles. In parallel, both natural and synthetic rheology modifiers were evaluated to achieve the target viscosity required for effective knife coating application. All suspensions demonstrated compatibility with the knife coating system.

3.1.2. Determining Suitable PHBHHx Concentration for Knife Coating Applications on Textiles

To determine the optimal PHBHHx concentration for textile coating applications, formulations containing 5% to 20% *w/v* of the polymer were prepared, as previously described. All formulations included additives. At the initial stage, xanthan gum, a natural rheology modifier, was incorporated into each formulation to achieve the viscosity necessary for an effective knife coating. The influence of PHBHHx concentration on the final coating performance was evaluated through surface morphology, wettability, and thickness analyses of the coated textile substrates. The corresponding results are summarized in Figure 1 and Table 1, respectively.

Table 1. Thicknesses and water contact angle measurements on knife-coated fabrics with different PHBHHx concentrations (5–20% *w/v*), both with and without thermal treatment.

% PHBHHx	Treatment	Thickness (mm)	Contact Angle (°) ± S.D.
5	Without hot pressing	0.70 ± 0.01	76.6 ± 38.9
	Hot Pressing (180 °C)	0.66 ± 0.02	84.9 ± 13.5
10	Without hot pressing	0.79 ± 0.00	81.7 ± 9.0
	Hot Pressing (180 °C)	0.65 ± 0.00	63.3 ± 7.9
15	Without hot pressing	0.88 ± 0.01	81.7 ± 10.1
	Hot Pressing (180 °C)	0.73 ± 0.01	69.5 ± 14.8
20	Without hot pressing	0.91 ± 0.00	81.6 ± 10.3
	Hot Pressing (180 °C)	0.74 ± 0.01	69.1 ± 10.7

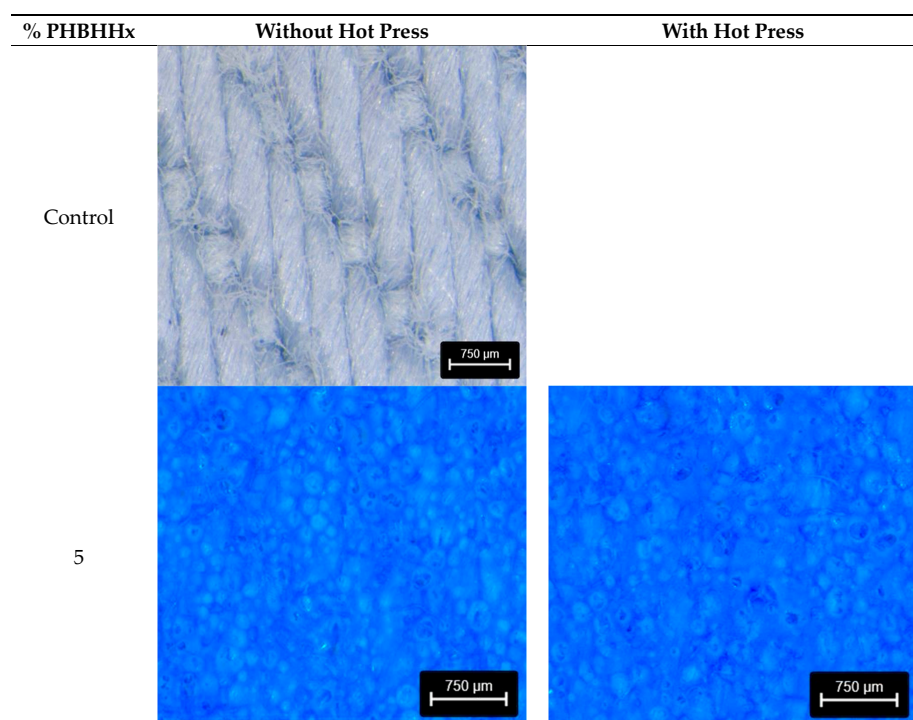


Figure 1. Cont.

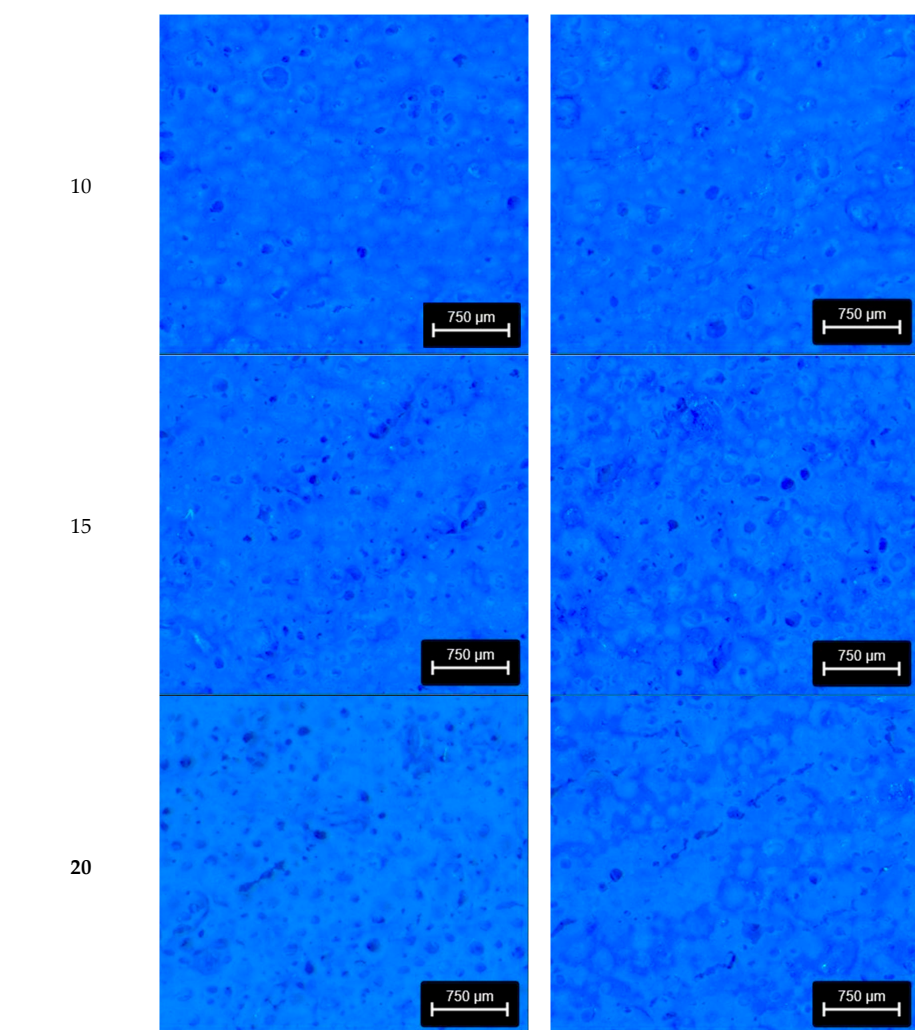


Figure 1. Optical microscopy images of textile coatings prepared with varying PHBHHx concentrations, captured using a Leica Lupa FX272 stereomicroscope (Leica Microsystems GmbH, Wetzlar, Germany) at 12.5× magnification.

The control corresponding to the cotton fabric shows the typical surface morphology of cotton. No image was included for the hot-pressing process, as cotton is a non-thermoplastic material and, therefore, no significant surface changes were expected. Surface analysis of the coating revealed that those containing 10% *w/v* PHBHHx exhibited the most uniform surface coverage, despite minor textural irregularities. In contrast, the 5% PHBHHx formulation resulted in significant surface non-uniformity and visible discontinuities, likely due to insufficient polymer content for effective film formation. At higher concentrations (15% and 20% *w/v*), an increased presence of entrapped air bubbles was observed, with the 20% formulation showing the most pronounced defects. These findings suggest that excessive polymer content may hinder coating uniformity due to increased viscosity and air entrapment during application.

Regarding coating thickness (Table 1), measurements showed a proportional increase with higher polymer concentrations, reflecting the greater polymeric content in the formulations, from 0.70 ± 0.01 mm for 5% PHBHHx to 0.91 ± 0.00 mm for 20% PHBHHx. After hot pressing, all samples exhibited a slight reduction in thickness, attributed to polymer compaction and improved film adhesion to the textile substrate.

With respect to the effect of thermal treatment, its application reduced the presence of entrapped air bubbles across all samples, thereby enhancing surface homogeneity. However, some surface irregularities remained visible even after treatment. Overall, these findings

indicate that a 10% PHBHHx concentration offers the best compromise between coating uniformity, thickness stability, and defect minimization.

To complement the surface analysis, the wettability of the different knife-coated fabrics was evaluated through static contact angle measurements (Table 1). Under all tested conditions, the coatings exhibited a hydrophilic surface character, with contact angles consistently below 90° . Despite the varying PHBHHx concentrations, the hydrophilic character can be attributed to the presence of hydrophilic additives (Tween 20 and Dysperbyk 190), as well as the rheological agent xanthan gum, a natural polysaccharide rich in hydroxyl groups that promotes strong hydrogen bonding interactions with water [25]. Notably, samples containing 10%, 15%, and 20% PHBHHx exhibited similar contact angle values in the absence of thermal treatment ($\approx 82^\circ$), indicating that increasing the polymer concentration beyond 10% does not substantially enhance hydrophobicity. Therefore, a concentration of 10% can be considered the threshold of the performance plateau, representing the optimal concentration for achieving a good performance among those tested. In contrast, the 5% PHBHHx formulation exhibited a comparable mean contact angle (76.6°) but a significantly higher standard deviation ($\pm 38.9^\circ$), indicating poor coating uniformity. This finding aligns with the morphological observations presented in Figure 1. This high standard deviation is likely due to the insufficient polymer content, which may hinder the formation of a continuous and cohesive film across the textile surface. Notably, thermal treatment significantly improved the uniformity of this formulation, reducing the contact angle standard deviation to $\pm 13.5^\circ$. This underscores the role of hot pressing in enhancing homogeneity, particularly at lower polymer concentrations.

However, at higher concentrations, thermal treatment resulted in a reduction in the average contact angle. These findings suggest that, at intermediate polymer concentrations, the combination of sufficient polymer content and thermal treatment may enhance polymer chain mobility, promoting surface leveling or the reorientation of hydrophilic functional groups, ultimately leading to increased surface hydrophilicity. Among all tested conditions, the 10% PHBHHx formulation was identified as the most effective, providing an optimal balance between material efficiency, coating uniformity, and wettability performance. However, when considering broader applications in footwear, especially for external uses, the inherently hydrophilic nature of the developed coating may limit its water resistance. To overcome this limitation and explore the tunability of surface properties, particularly hydrophobicity, additional formulations containing 10% PHBHHx were developed. These new formulations were prepared using different strategies, by omitting hydrophilic additives, and by replacing the natural thickener, xanthan gum, by a synthetic-based thickener, Tubicoat Verdicker LP. These formulations are evaluated in the following sections.

3.1.3. Effect of a Synthetic Rheology Modifier and Additive Absence on the Performance of 10% PHBHHx Knife-Coated Fabrics

Among the coatings initially evaluated, the 10% PHBHHx knife-coated fabrics exhibited the most uniform and consistent surface morphology, achieving the highest material efficiency relative to functional performance, as detailed in the preceding section. Nonetheless, there remains potential to further improve both coating uniformity and surface hydrophobicity. As previously discussed, new formulations containing 10% PHBHHx were developed without hydrophilic additives (Tween 20 and Dysperbyk 190) and employed an alternative synthetic-based thickener, Tubicoat Verdicker LP. The viscosity of the developed formulations was evaluated, yielding values of approximately 9000 cP for the additive-free system and 13,400 cP for the formulation containing hydrophilic additives. These values fall within the typical range expected for knife-coating applications, which generally require viscosities between 5000 and 20,000 cP to ensure adequate film formation, coating uniformity, and controlled penetration into textile substrates [26]. The

observed increase in viscosity with the addition of hydrophilic components is consistent with the expected behaviour of such additives, which tend to enhance polymer–polymer and polymer–solvent interactions. This results in higher resistance to flow, improving coating stability and application control. Overall, the measured viscosities confirm the processability of these formulations and their suitability for textile coating operations.

Subsequently, a comprehensive evaluation was carried out to assess the impact of these formulation modifications on coating performance and material functionality. This included surface analysis, contact angle measurements to evaluate surface wettability, air and water vapor permeability testing, as well as assessments of abrasion and wash resistance. A standardized hot pressing protocol was applied across all formulations to investigate the contribution of thermal consolidation to coating performance. For comparative purposes, parallel analyses were also conducted on samples that had not undergone hot pressing, allowing for a systematic evaluation of the influence of thermal treatment on the structural and functional properties of the coatings. This experimental design enabled a systematic evaluation of how formulation composition, specifically the presence or absence of surfactant additives and the type of rheology modifier, combined with thermal processing, influenced the structural integrity and functional performance of PHBHHx-based textile coatings.

3.2. Characterizations of Aqueous 10% PHBHHx Knife Coatings

3.2.1. Surface and Thickness Analysis

Surface analysis was conducted to evaluate the morphological characteristics of cotton fabrics coated with PHBHHx formulations. The presence of additives markedly enhanced surface uniformity, producing more homogeneous and continuous coatings that also exhibited the lowest measured thicknesses (0.71 ± 0.01 mm, without hot pressing). In contrast, the formulation without additives and without thermal treatment presented a markedly irregular surface and higher thickness, characterized by discontinuities and poor film formation. This increase in irregularities and apparent thickness is likely due to insufficient flow and leveling of the polymer matrix during coating, leading to localized accumulation of material in uneven regions.

It is worth noting that no substantial differences in thickness were observed between coatings produced with the natural thickener (xanthan gum) 0.79 ± 0.00 mm and the synthetic thickener (Tubicoat Verdicker LP) 0.71 ± 0.01 mm at 10% *w/v* PHBHHx when additives were present. However, coatings containing additives consistently showed slightly lower thickness values. This behavior can be attributed to the ability of surfactant-type additives (such as Tween 20 and Disperbyk 190) to improve polymer chain mobility and reduce surface tension at the coating–air and coating–substrate interfaces. As a result, the coating spreads more effectively across the textile surface, forming a thinner and more uniform layer. Additionally, enhanced wetting promoted by the additives facilitates better penetration of the polymer into the textile interstices, contributing to a reduction in apparent film thickness.

Upon application of thermal treatment (hot pressing), both additive-containing and additive-free formulations demonstrated improved surface regularity accompanied by a reduction in thickness. This effect suggests that hot pressing increases polymer chain mobility and alignment, allowing the molten material to redistribute more evenly and adhere more effectively to the textile fibers. The combined influence of additives and thermal treatment is therefore critical for minimizing surface defects, achieving uniform coating coverage, and controlling the final thickness of the PHBHHx-based coatings.

3.2.2. FTIR Analysis

The FTIR spectra of uncoated cotton fabric, PHBHHx polymer powder, and PHBHHx-coated cotton fabrics are shown in Figure 2. The primary objective of this analysis was to confirm the successful deposition of the polymer onto the textile substrates and to assess the effect of hot pressing in comparison to samples not subjected to heat treatment.

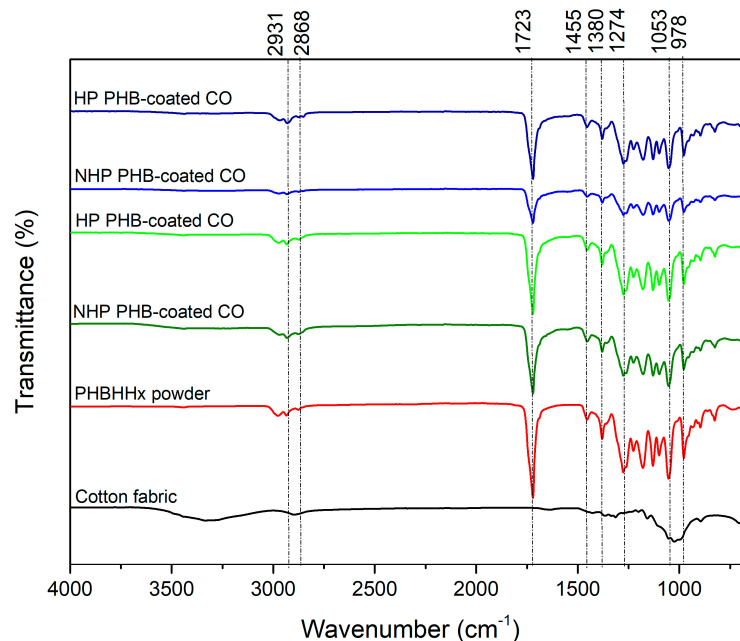


Figure 2. ATR-FTIR spectra of uncoated cotton fabric, PHBHHx polymer powder, and PHBHHx-coated cotton fabrics with and without hot pressing. Green spectra represent coatings formulated with additives, while blue spectra correspond to coatings without additives. Samples are labeled as NHP (non-hot-pressed) and HP (hot-pressed) to indicate the absence or presence of thermal treatment, respectively.

The spectrum of the uncoated cotton fabric clearly displays characteristic absorption bands associated with its cellulosic nature. A strong band at 1030 cm^{-1} corresponds to C–O stretching vibrations in the polysaccharide backbone, while the peak at 892 cm^{-1} is attributed to the β -glycosidic linkage, both serving as distinctive markers of cellulose structure [27,28]. Regarding to FTIR spectrum of PHBHHx powder exhibits the typical absorption bands of polyhydroxyalkanoates (PHAs). The most prominent peak, at approximately 1723 cm^{-1} , is associated with the C=O stretching vibration of ester carbonyl groups, a key fingerprint of the aliphatic polyester backbone [29]. Additional well-defined bands appear at around 2931 cm^{-1} and 2876 cm^{-1} , attributed to the asymmetric and symmetric stretching of $-\text{CH}_3$ and $-\text{CH}_2$ groups, respectively, from the alkyl side chains. A cluster of peaks between 1000 and 1300 cm^{-1} , particularly the one at 1278 cm^{-1} , is assigned to C–O–C stretching and CH bending vibrations, confirming the presence of ester linkages and methylene groups. Within this region, the peak at 1053 cm^{-1} corresponds to C–O stretching, while the band around 978 cm^{-1} is attributed to weaker C–C skeletal vibrations associated with the polymer backbone. Additionally, bands at 1455 cm^{-1} and 1380 cm^{-1} are assigned to $-\text{CH}_2$ scissoring and $-\text{CH}_3$ symmetric bending, respectively, characteristic features of PHAs [30,31].

These characteristic PHBHHx peaks are clearly observed in the spectra of knife-coated PHBHHx on cotton fabrics, confirming the successful deposition of the polymer onto the cellulosic substrates. No additional peaks were observed in the spectra of samples containing additives, nor did the application of heat treatment introduce any significant

spectral changes. This indicates that neither the incorporation of additives nor the post-coating hot pressing caused chemical modifications to the polymeric structure.

In summary, FTIR analysis confirms the presence of the PHBHHx polymer through its characteristic absorption bands and validates the successful deposition of the polymeric coating onto the cotton fabrics.

3.2.3. Wettability Analysis

Contact angle measurements were conducted to evaluate the surface wettability of the coated fabrics under different processing conditions, specifically, with and without additives, and with and without hot pressing. A summary of the results is provided in Table 2. The results indicate that both the presence and absence of additives, as well as the application of thermal treatment, significantly influence the hydrophilicity of the coatings, particularly highlighting the role of additives in modulating surface wettability. The addition of additives led to a notable reduction in the contact angle, indicating enhanced surface hydrophilicity. Specifically, in the absence of hot pressing, the contact angle decreased from 121.1° (without additives) to 93.6° (with additives). When hot pressing was applied, this effect was further amplified, the contact angle dropped from 110.5° (without additives) to 76.0° (with additives), representing the most hydrophilic and uniform surface among all samples tested.

Table 2. Water contact angle measurements of cotton fabrics coated with 10% PHBHHx, comparing samples with and without additives and with and without thermal treatment (hot pressing).

Sample	Additives/Thermal Treatment	Contact Angle (°) ± S.D.
10% PHBHHx-coated cotton fabric	With/Without	93.6 ± 14.3
	With/With	76.0 ± 3.7
	Without/Without	121.1 ± 10.7
	Without/With	110.5 ± 13.5

Analysis of the results indicates that hot pressing contributed to improved wettability of the coatings, albeit to a lesser extent than the incorporation of additives. This effect may be attributed to the reduction in micro- and nanoscale surface roughness, which, according to the Cassie–Baxter model, typically enhances hydrophobicity by trapping air pockets beneath water droplets, thereby increasing the apparent contact angle [32,33]. The surface smoothing induced by hot pressing likely attenuates this effect, as evidenced by the experimental results, thereby leading to a reduction in hydrophobicity. Additionally, hot pressing may promote the migration of additives toward the surface and induce molecular rearrangement within the coating, both of which can increase surface energy, as demonstrated also on study developed by Brogly et al. [34]. These changes collectively result in a more wettable surface, further decreasing the water contact angle. In the absence of additives, hot pressing reduced the contact angle from 121.1° to 110.5°, while in the presence of additives, it resulted in a significant decrease from 93.6° to 76.0°. However, it is important to highlight that the markedly lower standard deviation ($\pm 3.7^\circ$) observed in the sample containing additives and subjected to hot pressing suggests a more homogeneous surface coating, as also observed in surface analysis (Figure 3). This enhanced uniformity is likely attributed to the combined effects of the additives and thermal treatment, which together facilitate a more consistent distribution of the coating across the textile substrate. These findings highlight the importance of optimizing the formulations and processing parameters to achieve functional coatings with tailored surface characteristics.

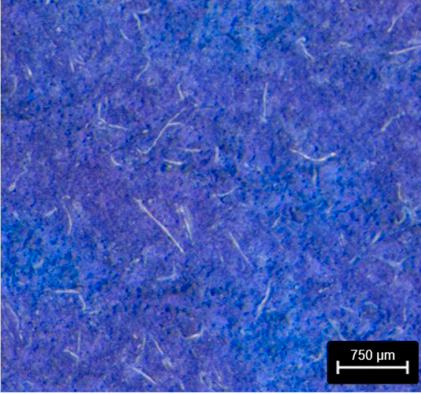
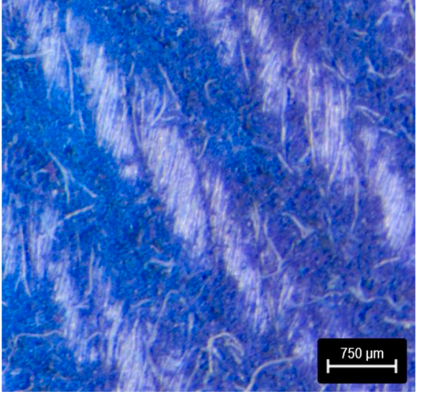
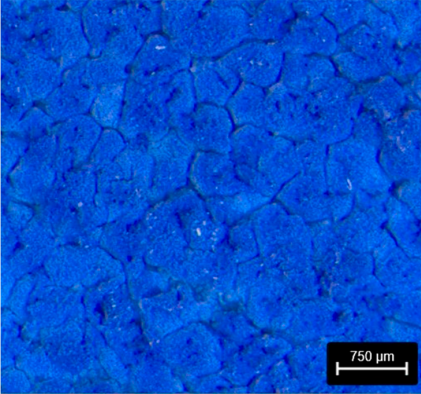
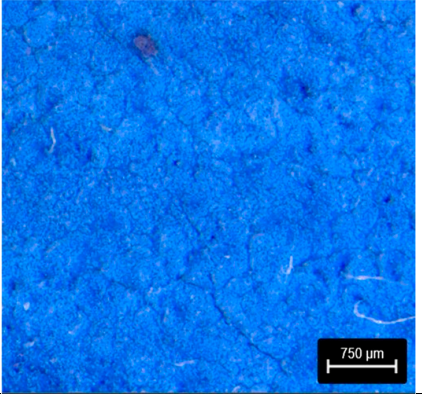
Additives	Without Hot Press	Thickness (mm)	With Hot Press	Thickness (mm)
Added		0.71 ± 0.01		0.61 ± 0.01
Non-added		0.80 ± 0.01		0.65 ± 0.05

Figure 3. Optical microscopy images of 10% PHBHHx knife-coated fabrics prepared with Tubi-coat Verdicker LP, with and without additives. Images were captured using a Leica Lupa FX272 stereomicroscope at $12.5\times$ magnification.

3.2.4. Permeability Analysis

The effects of PHBHHx coating, additive incorporation, and thermal treatment on the air permeability, water vapor permeability (WVP), and their respective retention indices (I%) of cotton fabrics are summarized in Table 3. These parameters are critical for maintaining thermophysiological comfort, particularly in footwear applications, where adequate breathability is essential to support moisture and heat regulation [35]. The uncoated control cotton fabric exhibited the highest air permeability ($94.0 \text{ L/m}^2/\text{s}$) and WVP ($669.8 \text{ g/m}^2/24 \text{ h}$), serving as the benchmark for breathable textile performance. This corresponds to a water vapor permeability retention index (I%) of 95.3%. Coating the fabric with 10% PHBHHx resulted in a significant decrease in both air and water vapor permeability, as clearly reflected by the retention index (%) values, independent of additive incorporation or the application of hot pressing. Among the coated samples, the fabric treated with additives and subjected to hot pressing exhibited a notable recovery in permeability, with air permeability increasing to $68.0 \text{ L/m}^2/\text{s}$, WVP rising to $651.0 \text{ g/m}^2/24 \text{ h}$, and a retention index of 92.6%. The elevated WVP values are strongly correlated with the lower contact angles observed, both of which are indicative of increased surface hydrophilicity. This suggests that the coating allows for greater interaction with water molecules, facilitating vapor transmission through the textile. Notably, the WVP values obtained for these samples closely resemble those of the uncoated cotton fabric, implying that the applied coating does not significantly hinder the material's inherent breathability. This outcome suggests that the combination of additives and thermal treatment promotes a more uniform and continuous coating layer (as also observed in the surface analysis, (Figure 3), likely by enhancing

polymer flow and distribution across the textile substrate while maintaining inter-fibre channels essential for vapor and air permeability. Additionally, hot pressing may facilitate the migration of additives toward the surface, potentially creating micro voids or pores that contribute to higher breathability. In contrast, the sample coated with additives but without hot pressing exhibited one of the lowest air permeabilities ($20.3 \text{ L/m}^2/\text{s}$) and a moderately reduced WVP ($398.1 \text{ g/m}^2/24 \text{ h}$), indicating that the polymer may have accumulated irregularly on the surface, partially obstructing fabric porosity. Notably, the absence of thermal treatment appears to limit the reflow and levelling of the coating, especially when additives are present.

Table 3. Air permeability, water vapor permeability (WVP), and Index values (I) of cotton control and 10% PHBHHx-coated cotton fabrics with and without additives and thermal treatment. Values are presented as mean $\pm$ standard deviation (S.D.).

Sample	Additives/Thermal Treatment	Air Permeability $\text{L}/(\text{m}^2/\text{s}) \pm \text{S.D.}$	WVP ($\text{g}/\text{m}^2/24 \text{ h}$) $\pm \text{S.D.}$	I (%)
Control cotton		94.0 ± 2.3	669.8 ± 12.1	95.3
10% PHBHHx-coated cotton fabric	With/Without	20.3 ± 4.7	398.1 ± 27.8	62.0
	With/With	68.0 ± 3.1	651.0 ± 5.4	92.6
	Without/Without	25.4 ± 1.9	510.7 ± 2.9	81.0
	Without/With	19.5 ± 4.4	245.6 ± 66.2	39.0

In the absence of additives, the sample without hot pressing exhibited slightly higher air and water vapor permeability compared to its hot-pressed counterpart. Specifically, air permeability was $25.4 \text{ L/m}^2/\text{s}$ and WVP reached $510.7 \text{ g/m}^2/24 \text{ h}$, whereas the hot-pressed sample showed reduced values of $19.5 \text{ L/m}^2/\text{s}$ and $245.6 \text{ g/m}^2/24 \text{ h}$, respectively. Correspondingly, the WVP retention index for the non-hot-pressed coating was 81%, significantly higher than the 39% observed for the thermally treated sample. This suggests that hot pressing, in the absence of additives, may negatively impact moisture permeability, an effect further evidenced by the increased hydrophobicity, as indicated by the higher contact angle values observed. This suggests that thermal treatment without additives may cause excessive compaction or surface sealing of the PHBHHx layer, severely limiting vapor transport. Furthermore, the high standard deviation observed in this latter sample's WVP indicates poor coating uniformity, possibly due to polymer phase separation or uneven redistribution during hot pressing.

Overall, these results demonstrate that, while PHBHHx coatings inherently reduce fabric breathability compared to uncoated cotton, the judicious use of additives in combination with hot pressing can partially mitigate this effect. Notably, the chemical composition of the coating exerts a stronger influence on permeability than the coating thickness alone. For instance, the formulation without additives and without hot pressing exhibited the greatest thickness among the samples analysed (Figure 3), yet it simultaneously displayed the highest WVP and only moderate air permeability. This apparent paradox can be explained by the presence of defects and discontinuities in the coating, as revealed by morphological analyses. In other words, despite its greater thickness, structural irregularities created additional pathways for water vapor and air transport, leading to increased permeability. Coatings subjected to hot pressing were more compact, resulting in slightly reduced thicknesses. Nevertheless, even among these more uniform coatings, WVP values varied considerably, further emphasizing the predominant role of coating chemistry in governing permeability. These findings underscore that both formulation chemistry and processing conditions are critical determinants of the functional performance of coated textiles. By

carefully optimizing these parameters, it is possible to produce PHBHHx-coated fabrics that retain adequate air and WVP, rendering them suitable for breathable and functional applications, including footwear linings, uppers, and protective textiles.

3.2.5. Abrasion Resistance

The abrasion resistance of cotton fabrics coated with 10% PHBHHx was evaluated using the Martindale abrasion test, conducted up to 51,200 cycles in accordance with ISO 5470-2:2021. The results, summarized in Table 4, demonstrate that the developed coatings exhibit excellent mechanical durability under repeated mechanical stress.

Table 4. Abrasion resistance (Martindale) of coatings with 10% PHBHHx according to ISO 5470-2:2021.

Sample	Additives/Thermal Treatment	Degree of Specimen Degradation
10% PHBHHx-coated cotton fabric	With/Without	0
	With/With	0
	Without/Without	1
	Without/With	0

Notably, samples containing additives, regardless of thermal treatment, showed no visible degradation (grade 0) throughout the test, indicating superior abrasion resistance. This highlights the crucial role of additives in enhancing coating integrity, likely through improved polymer flexibility and stronger interfacial interactions with the textile substrate. The absence of significant differences between hot-pressed and non-hot-pressed samples with additives suggests that additive incorporation alone is sufficient to stabilize the coating under abrasion.

Interestingly, the sample without additives but subjected to hot pressing also maintained a grade 0 rating, suggesting that thermal treatment alone contributes significantly to abrasion resistance. This effect can be attributed to the densification and reorganization of the polymer matrix during hot pressing, which likely produces a smoother, more cohesive film structure that resists mechanical wear. In contrast, the sample without additives and without hot pressing exhibited slight degradation (grade 1), indicating early signs of wear. This observed reduction in durability is likely due to poorer film uniformity, weaker adhesion to the substrate, and microstructural defects, as confirmed by surface analysis (Figure 3).

These findings highlight the distinct roles of additive incorporation and thermal consolidation in improving the mechanical wear resistance of PHBHHx coatings, an essential requirement for footwear component applications.

3.3. Washing Resistance

To evaluate the washing durability of PHBHHx-based coatings and elucidate the effects of laundering on their structural and surface properties, detailed surface morphology and wettability analysis were performed. Across all tested coated fabrics, the PHBHHx coatings demonstrated considerable washing resistance, as evidenced by the retained presence of the polymeric layer on the textile surface even after five laundering cycles, as shown in Figure 4.

Post-washing surface images revealed that thermally treated samples retained a more cohesive and continuous coating layer. In some cases, dispersed polymer granules were observed on textile structure, further indicating effective film retention.

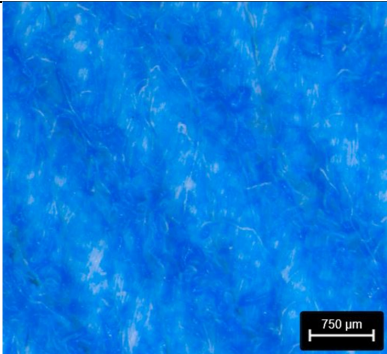
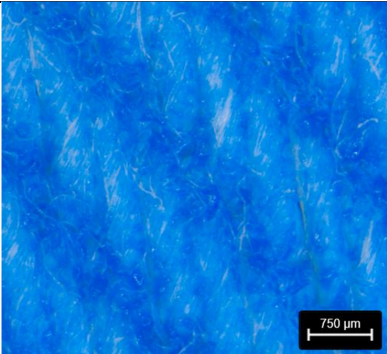
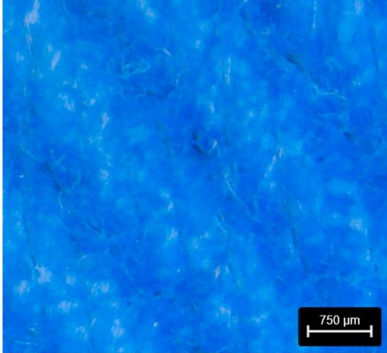
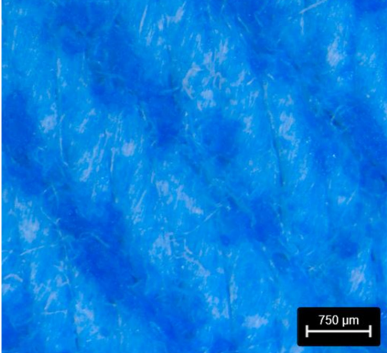
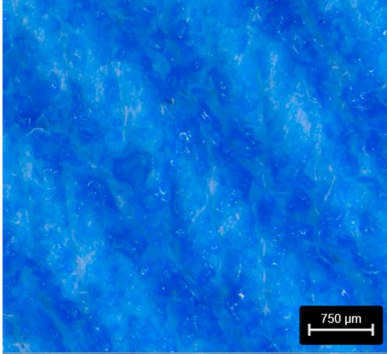
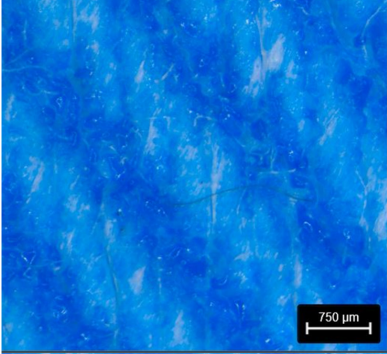
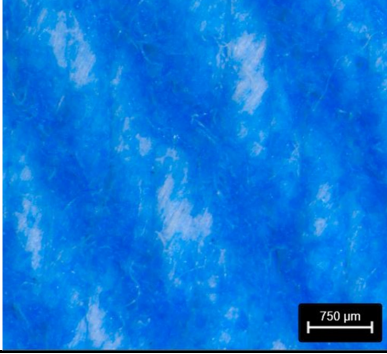
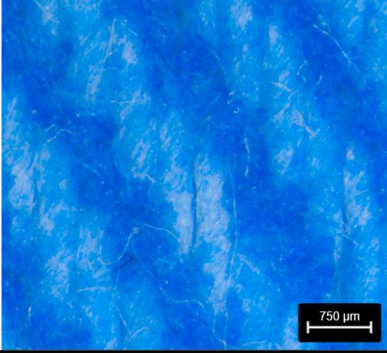
Additives	Number of washings	Without Hot Press	With Hot Press
Added Non-added	1		
			
Added Non-added	5		
			

Figure 4. Optical microscopy images of 10% PHBHHx knife-coated fabrics, prepared with Tubicoat Verdicker LP, both with and without additives, after one and five washing cycles. Images were captured using a Leica Lupa FX272 stereomicroscope at 12.5× magnification.

However, comparative analysis between the first and fifth wash cycles revealed partial removal of the coating, particularly in samples without additives. This was indicated by increased exposure of the underlying cotton structure, suggesting progressive erosion or localized delamination of the polymeric film. These findings highlight the critical role of both additive incorporation and thermal treatment in improving the long-term adhesion, durability, and functional stability of PHBHHx coatings for textile applications. Regard-

ing to the thicknesses, they increased slightly after successive washing cycles (Table 5), primarily due to swelling of the PHBHHx matrix, fibre expansion, and formation of microstructural defects such as microcracks or surface roughening. Coatings with additives and/or hot pressing were initially more uniform and compact, showing smaller thickness increases, whereas additive-free or non-hot-pressed coatings, which contained more defects, exhibited more pronounced thickening. These findings indicate that post-wash thickness changes arise from structural rearrangements rather than additional material deposition, emphasizing the importance of formulation chemistry and processing in controlling coating stability.

Table 5. Water contact angle measurements of cotton fabrics coated with 10% PHBHHx, comparing samples with and without additives, and with or without thermal treatment (hot pressing), after one and five washing cycles.

Sample	Additives/Thermal Treatment	Contact Angle (°) ± S.D.			Thicknesses (mm)	
		Without Washings	1 Wash Cycle	5 Wash Cycles	1 Wash Cycle	5 Wash Cycles
10% PHBHHx-coated cotton fabric	With/Without	93.6 ± 14.3	93.6 ± 7.7	Absorbed instantly	1.04 ± 0.03	1.31 ± 0.06
	With/With	76.0 ± 3.7	88.0 ± 9.6	119.1 ± 6.8	0.90 ± 0.03	0.96 ± 0.02
	Without/Without	121.1 ± 10.7	106.4 ± 4.5	88.9 ± 8.1	1.11 ± 0.02	1.18 ± 0.06
	Without/With	110.5 ± 13.5	122.4 ± 22.7	99.5 ± 6.0	1.01 ± 0.05	0.95 ± 0.03

In addition to surface morphology analysis, ATR-FTIR spectroscopy was conducted to evaluate the chemical composition of the coated cotton fabrics after one and five washing cycles (Figure 5). The objective was to assess whether the PHBHHx polymer layer remained on the fabric surface following repeated laundering. The spectra shown correspond to samples after the first wash (a) and after the fifth wash (b). In all cases, the characteristic absorption bands of PHBHHx are clearly observed, regardless of whether the samples underwent hot pressing. This consistent spectral profile confirms the presence of the PHBHHx coating even after multiple washing cycles, indicating strong adhesion to the cotton substrate and good washing durability.

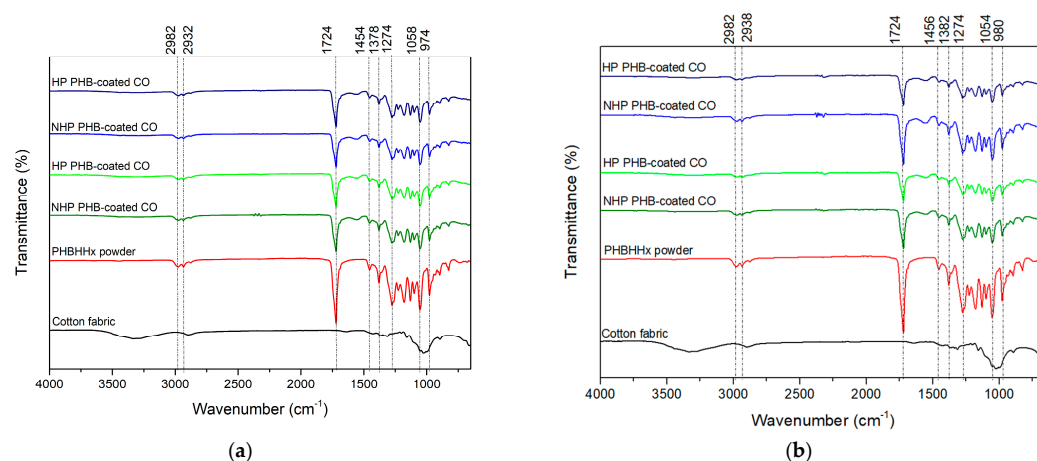


Figure 5. ATR-FTIR spectra of uncoated cotton fabric, PHBHHx polymer powder, and PHBHHx-coated cotton fabrics subjected to washing cycles, with and without hot pressing. (a) After the first wash; (b) After the fifth wash. Samples are labelled as NHP (non-hot-pressed) and HP (hot-pressed) to indicate the absence or presence of thermal treatment, respectively.

Table 5 presents the water contact angle values of 10% PHBHHx knife-coated fabrics, highlighting the effects of additive incorporation and thermal treatment (hot pressing) before and after one and five washing cycles. These measurements serve as indicators of surface hydrophobicity and, by extension, the structural integrity and durability of the coatings under laundering conditions.

Samples containing additives exhibited distinct behaviours depending on the application of thermal treatment. Without thermal treatment, the coating retained a relatively stable contact angle after one wash (93.6°) but lost hydrophobicity entirely after five cycles, with water absorbed instantly, indicating that additives alone are insufficient to protect the coating against wash-induced wear. In contrast, when additives were combined with thermal treatment, the initial contact angle was lower (76.0°) but progressively increased to 88.0° after one wash and 119.1° after five washes. This enhancement reflects reorganization and surface enrichment of the hydrophobic PHBHHx polymer, facilitated by the synergistic effect of thermal treatment and additives. The hydrophilic additives likely remain embedded in the bulk, while thermal consolidation promotes migration of PHBHHx chains toward the fibre surface, forming a continuous and resilient hydrophobic layer.

Among additive-free samples, the coating without thermal treatment exhibited the highest initial contact angle (121.1°) but decreased steadily to 88.9° after five washes, reflecting gradual deterioration. Thermal treatment alone improved wash durability, maintaining higher hydrophobicity (99.5° after five washes), highlighting its role in coating consolidation and adhesion even in the absence of additives.

Overall, these results demonstrate that thermal treatment is critical for maintaining and enhancing hydrophobicity in PHBHHx coatings during repeated washing, while the combination of additives and thermal consolidation produces a more resilient and adaptive surface suitable for functional textiles such as footwear components.

4. Conclusions

This study demonstrates the strong potential of PHBHHx-based coatings as sustainable and effective alternatives to conventional synthetic polymers and leather in footwear applications. Among the formulations tested, the 10% PHBHHx concentration delivered the best balance between material efficiency, coating uniformity, and surface functionality. The incorporation of hydrophilic additives combined with thermal treatment notably enhanced key properties such as wettability, vapor permeability, and durability. The synergistic effect of additives and hot-pressing improved water vapor transport and maintained long-term surface hydrophobicity, likely due to structural reorganization and additive migration during thermal treatment. This also contributed to the formation of microvoids that enhance breathability. Conversely, thermal treatment without additives caused surface compaction, reducing moisture permeability, as confirmed by increased contact angles. Hot pressing further strengthened coating-substrate adhesion, significantly boosting abrasion and washing resistance. These findings highlight the versatility and performance potential of PHBHHx coatings, positioning them as promising candidates for bio-based, breathable, and durable materials in next-generation sustainable footwear. Despite these advances, further optimization is needed to improve air permeability and water vapor transmission, crucial for meeting comfort standards in high-performance footwear. Current formulations approach the lower limits of typical breathable material benchmarks, 20 to 200 g/m²·24 h for water vapor permeability and 60 to 600 L/m²·s for air permeability but must advance to remain competitive. Overall, this work provides important insights into the roles of thermal treatment and additives in shaping coating morphology and function. It establishes a solid foundation for future research focused on systematic formulation refinement, process

control, and comprehensive performance evaluation to realize fully functional, market-ready PHBHHx coatings for sustainable footwear applications.

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