



M 2021

STUDY AND DEVELOPMENT OF COATING FORMULATIONS AND CONSEQUENT IMPACT ON THE CHARACTERISTICS OF THE FINAL PRODUCT

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MASTER DISSERTATION PRESENTED TO THE
FACULTY OF ENGINEERING OF UNIVERSITY OF PORTO IN
CHEMICAL ENGINEERING

Master in Chemical Engineering

Study and development of coating formulations and consequent impact on the characteristics of the final product

Master dissertation

of

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Developed within the course of dissertation

held in

Tintex Textiles, S.A.

T I N T E X NATURALLY
ADVANCED

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July 2021

Acknowledgment

I would first like to thank my supervisors Prof. Margarida Bastos, Prof. Fernão Magalhães, and Dr. Pedro Magalhães. They inspired me with their deep scientific knowledge and provided me valuable comments, remarks and all the support necessary throughout this master dissertation.

Furthermore, I would like to thank all the professors of the Integrated Master's in Chemical Engineering which gave me the critical knowledge over the years to carry out this dissertation.

I would also like to thank to the entire Tintex Textiles, S.A. team that welcomed me, especially Eng. Carlos Silva, Diana Alheira and Lucas Barros. To Eng. Carlos Silva for introducing me to the field of textiles and coatings and for his valuable guidance throughout the research, and to Diana Alheira and Lucas Barros for all the time they spent helping me and welcoming me in such a kind way.

I would like to acknowledge Dr. Diana Paiva from LEPABE, Dr. Sandra Monteiro from ARCP, and Mr. Luís Carlos Matos from the Chemical Engineering Department of FEUP for their availability and help in the use of FEUP equipment.

I would like to thank my family and boyfriend for the emotional support and for keeping me highly motivated. To my dog Kiara, thank you for the companionship and love, that were so important during this process.

To my friends who embarked with me on this journey, a special thank you for always believing in me. Your friendship was one of the greatest pillars of my academic success that culminated in this dissertation.

Professors Margarida Bastos and Fernão Magalhães, supervisors of this dissertation, are integrated members of LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, financially supported by: Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - funded by national funds through the FCT/MCTES (PIDDAC).

Abstract

Coated textiles have been gaining increasing importance, especially in the construction, medical, clothing, home furnishing, and protective textiles industries, and this market is expected to grow 4% by year until 2026. It is therefore important to research and develop new coating formulations. In addition, the urge around making the textile industry more sustainable has led companies to look for sustainability labels, with bluesign® standing out as the most looked-for and strict label.

The focal point of this dissertation was to study and develop a coating formulated only with bluesign® approved chemical substances and the consequent impact of this formulation on the characteristics of the final product. After the formulation was developed, it was applied as a paste or a stable foam, with different thicknesses, and in knits of different fibers (cotton and polyester). To study their performance characteristics and to understand the best way to continue the development of this product, textile quality control tests were employed (Martindale abrasion and pilling tests, dry and wet rubbing color fastness, Pilling Box test, wash resistance test, water resistance test, water repellency test, and air permeability test). A chemical, mechanical and morphological characterization (SEM, FTIR-ATR, Raman spectroscopy, DSC, TGA, and grab test) was performed in order to have a more in-depth understanding of the coating formulation and the final product. Furthermore, the coating formulation was improved, considering the information obtained from the quality control tests and the chemical characterization.

From the results obtained it can be concluded that the substrate has an influence on the performance characteristics since the polyester sample showed a higher water resistance and repellency than the cotton sample. On the other hand, the cotton sample presented a more pleasant hand feel. The coating thickness also turned out to be one major influencing parameter in the coating profilometry and consequently in the coating performance. The chemical characterization allowed a better understanding of the coating chemical composition and made it possible to conclude that the processing conditions were the most suitable. It was also possible to infer that the coating showed a good wettability of the surface, and consequently a good adhesion to the knit. The breaking strength of the knit was enhanced by the coating. The improvement of the coating formulation allowed an increase in the water resistance.

The work done set the foundation of bluesign® approved coating formulations of the company and the tests carried out contributed to a better understanding of how this project can be continued.

Keywords: bluesign®; coated textiles; polyurethane; cotton; polyester

Resumo

Os têxteis revestidos têm vindo a ganhar cada vez mais importância, especialmente nas indústrias da construção, medicina, vestuário, mobiliário e têxteis de proteção, e espera-se que este mercado cresça 4% por ano até 2026. Torna-se então importante a investigação e desenvolvimento de novas formulações de revestimento. Para além disso, a urgência em tornar a indústria têxtil mais sustentável tem levado as empresas a procurar certificados de sustentabilidade, com a bluesign® destacando-se com o certificado mais procurado e rigoroso.

O foco desta dissertação foi estudar e desenvolver um revestimento formulado apenas com substâncias químicas aprovadas pela bluesign® e o consequente impacto dessa formulação nas características do produto final. Após o desenvolvimento da formulação, o revestimento foi aplicado sob a forma de pasta ou espuma estável, com diferentes espessuras, e em malhas de diferentes fibras (algodão e poliéster). Para estudar o seu desempenho e entender a melhor direção para o desenvolvimento deste produto, foram realizados testes de controlo de qualidade têxtil (testes de abrasão e pilling - método Martindale, teste da solidez dos tintos à fricção (seco e húmido), método do “Pilling Box”, teste de resistência à lavagem, teste de resistência à água, teste de repelência à água e teste de permeabilidade ao ar). Foi também realizada uma caracterização química, mecânica e morfológica (SEM, FTIR-ATR, espectroscopia Raman, DSC, TGA e teste de tração) com vista a obter um conhecimento mais aprofundado da formulação do revestimento e do produto final. Na fase final, a formulação do revestimento foi melhorada, considerando as informações obtidas nos testes de controlo de qualidade e na caracterização química.

Pelos resultados obtidos pode-se concluir que o substrato tem influência no desempenho do produto final, uma vez que a amostra de poliéster apresentou maior resistência e repelência à água do que a amostra de algodão. Por outro lado, a amostra de algodão apresentou um toque mais agradável. A espessura do revestimento também mostrou ser um dos principais parâmetros influentes na perfilometria do revestimento e, consequentemente, no seu desempenho. A caracterização química permitiu uma melhor compreensão da composição química do revestimento e concluir que as condições de processamento usadas foram as mais adequadas. Também foi possível inferir que o revestimento apresentou uma boa adesão à malha. A resistência à rotura da malha foi reforçada pelo revestimento. O aperfeiçoamento da formulação permitiu um aumento da resistência à água.

O trabalho realizado permitiu definir a base de futuras formulações de revestimento da empresa aprovadas pela bluesign® e os testes realizados contribuíram para uma melhor compreensão de como este projeto poderá ser continuado.

Palavras-chave: bluesign®; têxteis revestidos; poliuretano; algodão; poliéster

Declaration

I hereby declare, under word of honor, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source.

Mariana Alves

July 5, 2021

Index

1	Introduction.....	1
1.1	Framing and presentation of the work	1
1.2	Tintex Textiles, S.A.	2
1.3	Contribution of the author to the work	3
1.4	Organization of the dissertation	3
2	Context and State of the art.....	5
2.1	Introduction to textile coatings	5
2.2	Coatings raw materials.....	6
2.2.1	Binders	7
2.2.2	Crosslinking agents	7
2.2.3	Pigments	8
2.2.4	Solvents	9
2.2.5	Additives	9
2.3	Waterborne coating formulations.....	11
2.3.1	Waterborne polyurethane dispersions	12
2.3.2	Waterborne acrylic dispersions	14
2.4	Substrate and coating interactions	15
2.5	Coating methods	18
2.6	bluesign® label	19
3	Materials and Methods	23
3.1	Materials.....	23
3.2	Methods.....	23
3.2.1	Preparation of the coating samples	23
3.2.2	Quality control tests.....	27
3.2.3	Chemical, mechanical and morphological characterization	28
4	Results and discussion	31
4.1	Pre-qualifying tests.....	31

4.2	Quality control tests.....	32
4.3	Chemical, mechanical and morphological characterization	34
4.3.1	Scanning Electron Microscopy	34
4.3.2	Fourier Transform Infrared - Attenuated Total Reflectance.....	34
4.3.3	Raman spectroscopy	39
4.3.4	Thermal analysis	40
4.3.5	Breaking strength	42
4.4	Validation of bluesign® product requirements.....	43
4.5	Coating formulation improvement.....	43
5	Conclusion.....	45
6	Assessment of the work done	46
6.1	Objectives Achieved.....	46
6.2	Limitations and Future Work	46
6.3	Final Assessment	46
7	References	47
Appendix A	Processes implemented by Tintex Textiles, S.A.	51
Appendix B	Equipment used during the course of the dissertation	54
Appendix C	SEM analysis of the knits.....	60
Appendix D	FTIR-ATR spectra of the knits	61
Appendix E	FTIR-ATR spectra of the CO_0.1 and PES_0.1 samples	66
Appendix F	Confocal Raman imaging.....	67

List of Figures

Figure 1 - Formation and stabilization of foam in a liquid. Adapted from [18].	10
Figure 2 - Schematic representation of emulsion polymerization. Adapted from [23].	12
Figure 3 - Reaction between a diisocyanate (MDI) and a polyol (EG) to form polyurethane. Adapted from [26].	12
Figure 4 - Polymerization reaction for acrylic resins. Adapted from [14].	14
Figure 5 - Illustration of textile fabrics: (A) woven structure, (B) weft-knitted structure, (C) warp-knitted structure. Adapted from [10].	16
Figure 6 - Representation of the interfacial tensions and contact angle of the coating system. Adapted from [33].	17
Figure 7 - Coating/textile surface coverage having a (A) poor wettability and (B) good wettability. Adapted from [33].	17
Figure 8 - Schematic representation of knife-over-roller coating. Adapted from [10].	18
Figure 9 - Schematic representation of rotary screen coating: (1) Screen, (2) Squeegee, (3) Counterpressure roll, (4) Rubber mat. Adapted from [34].	19
Figure 10 - Configuration of the calender rolls. Adapted from [34].	19
Figure 11 - Rating criteria of the bluesign® system. Adapted from [6].	21
Figure 12 - Quality control equipment: (A) Nu-Martindale Abrasion and Pilling tester; (B) Automatic Hydrostatic Head Tester FX 3000 HydroTester IV.	29
Figure 13 - Chemical characterization equipment: (A) VERTEX 70 FTIR spectrophotometer; (B) WITec Alpha300 R Micro-Raman.	30
Figure 14 - CO _{0.5} sample, where (A) is the uncoated part and (B) is the coated part.	32
Figure 15 - Coating applied on a blue knit, where (A) is the uncoated part and (B) is the coated part.	32
Figure 16 - SEM images of the coating surface on (A) PES _{0.5} , and (B) CO _{0.5} samples with a magnification of 300x.	35
Figure 17 - Cross-sectional images of the CO _{0.5} sample at different magnifications: (A) 300x and (B) 800x.	35
Figure 18 - Tintex paste coating (0.2 mm application thickness) SEM (A) surface and (B) cross-sectional images with a magnification of 200x.	35
Figure 19 - Normalized FTIR-ATR spectra of the CO _{0.5} , PES _{0.5} , and coating by itself samples.	36

Figure 20 - Normalized second derivatives of the spectra of the CO_0.1, CO_0.5, treated cotton knit, and coating by itself samples in the regions between (A) 2500 cm ⁻¹ and 3500 cm ⁻¹ , and (B) 700 cm ⁻¹ and 1800 cm ⁻¹	37
Figure 21 - Normalized second derivatives of the spectra of the PES_0.1, PES_0.5, treated polyester knit, and coating by itself samples, in the regions between (A) 2500 cm ⁻¹ and 3000 cm ⁻¹ , and (B) 700 cm ⁻¹ and 1800 cm ⁻¹	37
Figure 22 - Raman depth-profiling images of the samples (A) CO_0.5 and (B) PES_0.5.	39
Figure 23 - Raman spectra of the coating in the CO_0.5 and PES_0.5 samples.	40
Figure 24 - DSC curve of a sample of the coating by itself.	40
Figure 25 - Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of a sample of the coating by itself.	40
Figure 26 - DSC curve of the PES_0.5 sample.	41
Figure 27 - TG and DTG curves of the PES_0.5 sample.	41
Figure 28 - DSC curve of the CO_0.5 sample.	42
Figure 29 - TG and DTG curves of the CO_0.5 sample.	42
Figure 30 - Longitudinal (direction of the lengthwise loops) and transverse (direction of the crosswise loops) breaking strengths of the uncoated treated polyester and cotton knits, and the PES_0.5 and CO_0.5 samples.	42
Figure 31 - Sample of the improved formulation applied on the cotton knit SEM (A) surface and (B) cross-sectional images.	44
 Figure A-1 - Exhaust dyeing temperature profile. Adapted from [53].	52
Figure B-1 - METTLER TOLEDO precision balance.	54
Figure B-2 - IKA EUROSTAR 20 digital mechanical stirrer.	54
Figure B-3 - Thermo Scientific HAAKE Viscotester 2 Plus.	55
Figure B-4 - Werner Mathis Lab Coater&Dryer type LTE-S.	55
Figure B-5 - Teng FG20100 feeler gauge set with 20 blades (0.05 - 1.0 mm).	56
Figure B-6 - Monti Antonio roll calender model 93-2000sp.	56
Figure B-7 - MIB-Messzeuge outside micrometer.	56
Figure B-8 - James Heal Pilling Box.	57
Figure B-9 - Crockmeter.	57
Figure B-10 - James Heal Spray Rating Tester.	58

Figure B-11 - TEXTEST Air Permeability Tester FX 3300 LabAir IV.....	58
Figure B-12 - Thermo Fischer Scientific Phenom XL scanning electron microscope.	59
Figure B-13 - NETZSCH STA 449 F3 Jupiter.	59
Figure B-14 - NETZSCH DSC 214 Polyma calorimeter.	59
Figure C-1 - SEM images of (A) raw polyester knit, (B) treated polyester knit, (C) raw cotton knit, and (D) treated cotton knit.	60
Figure D-1 - Normalized FTIR-ATR spectra of the raw cotton knit and the treated cotton knit.	61
Figure D-2 - Molecular structure of cellulose (n = degree of polymerization). Adapted from [60].	61
Figure D-3 - Normalized second derivatives of the spectra of the treated and raw cotton knits in the region between (A) 2500 cm^{-1} and 3500 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1}	62
Figure D-4 - Poly(ethylene terephthalate) (PET) structure. Adapted from [61].	63
Figure D-5 - Normalized FTIR-ATR spectra of the raw polyester knit and the treated polyester knit.	63
Figure D-6 - Normalized second derivatives of the spectra of the treated and raw polyester knits in the region between (A) 2500 cm^{-1} and 3500 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1}	64
Figure E-1 - Normalized FTIR-ATR spectra of the CO_0.1, CO_0.5, treated cotton knit, and coating by itself samples.	66
Figure E-2 - Normalized FTIR-ATR spectra of the PES_0.1, PES_0.5, treated polyester knit, and coating by itself samples.	66
Figure F-1 - Raman imaging of the CO_0.5 sample: (A) Correlative Raman-SEM image; (B) Confocal color-coded Raman image of the area marked in (A).	67
Figure F-2 - Raman imaging of the PES_0.5 sample: (A) Correlative Raman-SEM image; (B) Confocal color-coded Raman image of the area marked in (A).	67

List of Tables

<i>Table 1 - Normal values of viscosity and density of the different application states</i>	<i>6</i>
<i>Table 2 - Coating compounds selected in the initial phase and in the formulation improvement</i>	<i>24</i>
<i>Table 3 - Characteristics of the selected coating compounds</i>	<i>24</i>
<i>Table 4 - Characteristics of the substrates used in the pre-qualifying tests</i>	<i>25</i>
<i>Table 5 - Drying, calendering, and polymerization conditions of the stable foam and paste</i>	<i>26</i>
<i>Table 6 - Codes attributed to each sample</i>	<i>26</i>
<i>Table 7 - Determination of the coating thickness in the final conditions</i>	<i>31</i>
<i>Table 8 - Rating of the quality control tests on a scale of 1-5.....</i>	<i>33</i>
<i>Table 9 - Results of the resistance to water, water repellency, and air permeability tests</i>	<i>33</i>
<i>Table 10 - Intensity peak ratios (normalized second derivative absorbance) of the CO_0.5, CO_0.1, PES_0.5, and PES_0.1 spectra</i>	<i>38</i>
 <i>Table D-1- Intensity peak ratios (normalized second derivative absorbance) of the treated and raw cotton knits spectra</i>	 <i>62</i>
<i>Table D-2 - Polyester knit finishing composition</i>	<i>63</i>
<i>Table D-3 - Intensity peak ratios (normalized second derivative absorbance) of the treated and raw polyester knits spectra.....</i>	<i>65</i>

Notation and Glossary

γ_L	interfacial tension between liquid and vapor	$\text{N}\cdot\text{m}^{-1}$
γ_S	interfacial tension between solid and vapor	$\text{N}\cdot\text{m}^{-1}$
γ_{SL}	interfacial tension between solid and liquid	$\text{N}\cdot\text{m}^{-1}$
m_{cup}	mass of the cup	g
$m_{cup+foam}$	mass of the cup filled with the foam	g
V_{cup}	volume of the cup	L

Greek Letters

θ	contact angle
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List of Acronyms

AATCC	American Association of Textile Chemists and Colorists
ASTM	American Society for Testing and Materials
CO INT	Cotton Interlock
CV	Coefficient of variation
DMPA	Dimethylolpropionic acid
DSC	Differential Scanning Calorimetry
DTG	Differential thermogravimetric
EG	Ethylene glycol
FEVE	Fluoroethylene vinyl ether
FTIR-ATR	Fourier Transform Infrared-Attenuated Total Reflectance
GOTS	Global Organic Textile Standard
GRS	Global Recycle Standard
HDI	1,6-hexamethylene diisocyanate
HEUR	Hydrophobically modified ethoxylated urethanes
IPDI	Isophorone diisocyanate
IR	Infrared
ISO	International Organization for Standardization
MDI	Methylene diphenyl diisocyanate

NMP	N-Methyl-2-Pyrrolidone
OCS	Organic Content Standard
PES INT	Polyester Interlock
PET	Poly(ethylene terephthalate)
PFAS	Per- and polyfluoroalkyl substances
PTMEG	Polytetramethylene ether glycol
PU	Polyurethane
TDI	Toluene diisocyanate
TG	Thermogravimetric
TGA	Thermogravimetric analysis
VOC	Volatile Organic Compound
WBPU	Waterborne polyurethane

1 Introduction

1.1 Framing and presentation of the work

The textile industry in Portugal is one of the largest, traditional and influential national business sectors. Nonetheless, in 2001, this sector saw a significant reduction in sales volume and employment due to the end of the derogation period of the Multifiber Arrangement. In order to react to this decline, the national industry started to invest in technological innovation and industrial know-how, leading to a strong recuperation of industrial activity since 2010.^[1] However, this increase in production, also favored by the emergence of fast fashion, has led to an increase in the environmental impact of this industry. For this reason, the national textile industry is currently focusing on the implementation of environmental and social sustainability principles.

The textile supply chain starts in the raw material extraction phase (the cradle stage), followed by the production of yarns and fabrics, dyeing and finishing of the textiles, and the clothing manufacturing process. The chain ends in the distribution, usage by the consumer and finally, the disposal (grave stage). Each one of these steps has a negative environmental impact, making this industry the second most polluting in the world, after the oil industry.^[2]

Tintex Textiles S.A. focuses on dyeing and finishing textiles, as well as other applications, like coatings. Conventionally, these processes use several chemicals that are hazardous for human health and the environment and end up contaminating water resources.^[3] For this reason, Tintex mostly opts for sustainable alternatives and their products can be granted with certifications such as GOTS, OCS, GRS, Standard 100 by OEKO-TEX®, and bluesign®.

The bluesign® holistic approach analyzes all input streams, from raw materials to chemical components and resources, to provide a textile product with a reduced ecological footprint along the entire supply chain without compromising the product functionality, quality, or design. Because it differentiates from other certifications that only evaluate the end product, this standard is one of the best-known and most strict sustainability labels within the textile industry.^[4]

The coating process is very recent compared to the other processes of the production and there is still little know-how on how to make it more environmentally friendly. During the coating lifetime, surface components can be released by wear, tear, laundering, photo-oxidation, and/or hydrolysis. For this reason, alternative polymers used in coating formulations, approved by bluesign®, should be used in order to stop the release of potentially harmful pollutants, but simultaneously deliver the same functionalities.^[5] On that premise, the main objective of this dissertation is to develop a coating formulation that is

fully bluesign® approved, in order to be able to produce a product that can be awarded the bluesign® label. At least 90% of a textile product (including the inner and outer layers of a garment including all prints) must be bluesign® approved to have the bluesign® label. In addition, 30% of all accessories such as zippers, buttons, and embroideries must be bluesign® approved.^[6]

The study of the coating formulation and consequently of the final product will be focused on the characterization in terms of its technical performance and, at a more fundamental level, recurring to chemical, mechanical and morphological techniques.

1.2 Tintex Textiles, S.A.

Tintex was founded by Mário Jorge Silva, in 1998, in Vila Nova de Cerveira, Portugal, providing services of dyeing and finishing textiles. Their motto “Naturally Advanced” positions the company as a leader in the sustainable textile industry, combining know-how and cutting-edge technology to establish relationships with their clients with an environment-driven approach. The company mainly sells its products to designers, R&D centers and fashion, athleisure, and lingerie brands.

Following the sustainable guideline, the company prioritizes the use of natural and regenerated fibers, such as organic cotton, wool, and lyocell. The liquid effluents generated during the various processes are treated in a wastewater treatment plant owned by the company. Regarding the residues generated during the production and auxiliary processes, another relevant environmental aspect, the company does the separation between industrial residues and residues similar to domestic residues, which are then sent to another company that does the valorization of these residues.

In such a competitive market, Tintex distinguishes itself for its innovation, creativity and constant will to improve its processes. For this reason, the company created a textile coating department in 2015 that has been growing ever since. Owing to the sustainability policy of Tintex, the coatings raw materials used are waterborne synthetic polyurethanes, including the various classes of polyols and isocyanates, creating a competitive advantage by offering the customer a product with high quality but with less environmental impact due to the non-use of organic solvents. This department also focuses on the integration of biopolymers and residues from other industries, such as cork, grape marc powder, and pine shell, thus contributing to the ideal of a circular economy.

1.3 Contribution of the author to the work

The development of this work allowed the creation of the first coating formulated only with bluesign® approved compounds in Tintex, with the possibility of receiving the bluesign® product label in the future, which is something that has been much requested by its clients due to the growing importance of this certification in the industry. This formulation can be the reference base for future bluesign® approved coating formulations developed in the company.

Furthermore, the studies carried out allowed a more in-depth comprehension of the impact that variables such as nature and structure of the substrate, coating's state of application, and coating's thickness, have on the technical performance of the product. In addition, it allowed Tintex to have a better perception of the surface and profilometry at microscopic level of the type of coatings the company typically develops.

1.4 Organization of the dissertation

This dissertation is divided into six chapters: Introduction, Context and State of the Art, Materials and Methods, Results and discussion, Conclusion, and Assessment of the work done.

In the first chapter - Introduction - it is performed an analysis of the evolution of the textile industry with a focus on the coated textiles industry. The issue of pollution in this industry and the growing importance of sustainability labels, such as bluesign®, are addressed, and it is explained the main objective of this dissertation.

In the second chapter - Context and State of the Art - it is initially presented the importance of coated textiles, the raw materials used in the formulation of coatings, a brief explanation of waterborne coating formulations, and the methods for coating's application. The chapter ends with an introductory reference to the bluesign® label.

In the third chapter - Materials and Methods - are described the materials utilized and the procedures adopted in the sample's preparation, quality control tests, and chemical and mechanical characterization.

In the fourth chapter - Results and discussion - is presented and discussed the obtained results from the methods described in the third chapter.

In the fifth chapter - Conclusion - is presented the relevant conclusions of the dissertation after the analysis of the obtained results.

In the sixth chapter - Assessment of the work done - is carried out an overall assessment of the work done, and it is presented proposals on how the project can be continued.

2 Context and State of the art

2.1 Introduction to textile coatings

A textile coating is a layer of a polymeric material deposited onto the textile and once it has been dried (and cured, if necessary), forms a bond with the fabric. The main purpose of the coating is to modify the textile surface in an attempt to improve its performance. Initially, the main function of textile coatings was for aesthetic and protection purposes but later evolved to create engineering textiles that interact with and respond to their environment, also known as smart textiles.^[7]

The market for textile coatings is expected to grow at a compound annual growth rate of 4% during the forecast period of 2016-2026 and the major growth drivers are the construction, medical, clothing, home furnishing, and protective textiles industries. Currently, the Asia Pacific accounts for the largest regional market and is also expected to register the fastest growth. Another relevant aspect is that thermoplastics are dominating the global textile coatings market, due to their lightweight nature, excellent insulating nature, and fire-retardant properties.^[8] In fact, the polymers used in Tintex coatings are all thermoplastics.

Current research on textile coatings includes materials development, improving and optimizing existing methods of application, combining multiple areas of technology such as nanotechnology, physics, biotechnology and biology, and improving environmental and economic impacts. Furthermore, the outbreak of the coronavirus pandemic (i.e., COVID-19) has drawn particular interest in the development of coatings with antiviral elements for the production of personal protective equipment, hygienic implements, and other devices to fight against viral pandemics.^[9]

Typical textile coatings are applied as a system with two or more layers, where at least one of the layers is the textile fabric and the other one is the continuous polymeric layer along with other additives. Each layer and their combination provide the desired textile properties. For example, the fabric mainly determines the strength, elongation, and dimensional properties of the system, whereas the polymeric coat provides properties such as the required resistance to penetration and impermeability, improving fabric abrasion, modifying the appearance for decorative purposes, among others.^[10]

In Tintex, most coating systems consist of two layers, the continuous polymeric layer and the textile substrate that is beforehand treated with hydrophilic and softening agents, as

well as technologies of thermo-setting (Appendix A), to give greater uniformity to the fabric surface and create a better adhesion of the coating to the substrate.

Typically, textile coatings formulations are mainly constituted by polymeric binder(s), crosslinkers, pigments, solvents, and other additives.^[11] The coating formulations are applied onto the textile surface in the form of an unstable foam, stable foam, or paste. What differentiates each one of these states is the amount of water and air added and retained in the interior of the solution, in the mixture phase. Ideally, air does not exist in the paste state. Regarding the foams, the quantity of air is adjusted accordingly to the final use. Unstable foams collapse during the drying process and the coating is almost completely absorbed by the substrate, providing a dry hand feel. The coating is applied as an unstable foam when it is necessary to give some functionality to the fabric (effect, hand feel, hydrophobicity), but it is intended to have a very discrete layer. Stable foams, as the name indicates, remain state stable, like a mousse/cream, over time. They usually yield a delicate touch to the textile surface and a higher air permeability than a paste, being its applicability very versatile. Unstable foams end uses include velour and automotive back coatings, and imitation suede, while stable foams are applied, for example, in black-out curtains or roller blinds, and breathable coatings for anoraks and rainwear. Paste applications are normally used in situations where a more resilient and impenetrable layer is needed, such as umbrellas, sportswear, and bag material.^[12]

Table 1 indicates the normal values of viscosity and density for each of these states. Regarding the foams, the density value presented refers to the density in the foam state, while the density of the paste is the density of the blend. Nevertheless, these values are merely indicative since it is possible to achieve different values of viscosity and density for each of these states by adapting the quantities of the polymers and additives.

Table 1 - Normal values of viscosity and density of the different application states

	Viscosity (dPa·s)	Density (g·L ⁻¹)
Unstable foam	1-5	~50
Stable foam	30-50	~250
Paste	≤100	~1000

2.2 Coatings raw materials

A wide range of polymers can be used in textile coatings and have an important role in the final characteristics of the coated textile. Functional characteristics such as chemical resistance, solvent resistance, acid resistance, alkali resistance, flame resistance, water

repellency or resistance, oil resistance, increased rigidity, abrasion resistance, tear resistance, good ability to stretch, high or low friction, and particular response to the surrounding environment, can be obtained through a proper selection of polymers, additives, and textile substrate. This selection depends on the melting point, glass transition temperature, molecular weight, mechanical and chemical properties of the polymers.^[10]

2.2.1 Binders

The main role of the binder in the overall coating formulation is to bind the functional ingredients, such as pigments and other additives, to form a film. The binder is usually composed of one or more polymers and in waterborne coatings, it usually comes in the form of waterborne dispersions.^[11]

Several criteria are relevant for the proper choice of the binder:^[13,14]

- High molecular weight or capability to crosslink after application of coatings;
- Soluble in solvents or dispersible in water;
- Capable of forming a continuous, adherent, and uniform film;
- Requirements of target property: gloss, hardness, color, solvent resistance, corrosion protection, etc.
- Broad range of compatibility with different binders, crosslinkers, additives, solvents, and water;
- Requirements for low or no volatile organic compounds (VOCs) for their processing and use in coatings;
- Preferably made from sustainable resources;
- Suitable for the application method selected;
- Able to offer a coating product that conforms with health and environmental requirements;
- Be cost-competitive.

This formulation component determines the permeability, mechanical properties, chemical resistance, and ultraviolet resistance of the coating and is responsible for a good adhesion to the substrate or other layers of the coating system. Usually used polymeric binders include rubbers, polyvinyl chloride, silicones, polyurethanes (PU), and acrylates.^[10]

2.2.2 Crosslinking agents

Coatings can obtain their integrity either by physical drying (that is simply solvent evaporation) or via crosslinking, usually by adding a crosslinking agent, which is a low molecular weight compound capable of reacting with an active group of the binders. Typical examples of crosslinkers are molecules with an amino, isocyanate, or a C=C functionality.

During crosslinking, linear polymer chains become covalently linked, creating a three-dimensional network structure. This makes the polymer insoluble and the mobility of the molecular chains decreases. In consequence, it hardens the coating and reduces the penetration of external molecules into the coating. Properties such as surface coverage, mechanical strength, chemical resistance, and thermal stability are also improved.^[13,15]

Polymer crosslinking can be achieved by the application of heat, pressure, change in pH, and radiation. As a result of crosslinking, an initial thermoplastic polymer is converted into a thermosetting polymer.^[15]

2.2.3 Pigments

The addition of color pigments, effect-inducing materials, and extenders offers the coating chroma, hiding power, special optical effects, but also functional properties such as corrosion resistance, resistance to UV light, and anti-fouling properties. The term pigment is often related to optical behavior, while the term extender (or filler) is related to protection and reinforcement.^[14,16]

Pigments are typically:^[13]

- White, colored, black, or fluorescent;
- Insoluble in the binder or solvent used;
- Dispersed in the binder in case of solvent-based and solventless coatings;
- Physically and chemically unaffected by other coating components;
- Capable of changing the coating appearance (e.g. by selective absorption and/or scattering of light).

Pigments can be classified based on color, as achromatic (white or black) or chromatic pigments, and based on their chemical nature, as organic or inorganic pigments. The organic pigments constitute mainly azo pigments, but phthalocyanine pigments are also often used. In the inorganic pigments, it is possible to distinguish the oxides, sulfides, chromates, molybdates, phosphates, and metallic and non-metallic elements. They consist of discreet particles, often crystalline in nature.^[14,17]

Extenders are a subdivision of inorganic pigments and their main task is to fill the coating spatially with skeletal material and therefore to influence the mechanical properties. They can influence the impact strength, swelling power, water vapor permeability, wear resistance, and sandability. The most common extender pigments are calcium carbonate, various silicates such as kaolin and talc, and barium sulfate.^[16,17]

2.2.4 Solvents

By definition, solvents are liquids comprising one or more components that are volatile under specific drying conditions and capable of dissolving binders without chemically reacting with them. Their primary role is to lower the viscosity of the binder for an easier application and better film formation thereafter due to evaporation. Nonetheless, another significant role of solvents is to control final film properties, by guaranteeing a balance between the flowability and leveling.^[14] Common organic solvents are aromatic hydrocarbons such as xylene and solvent naphtha, aliphatic hydrocarbons such as mineral spirit or vernice, esters such as ethyl acetate or butyl acetate, alcohols such as propanol or butanol, ethers such as butyl glycol, ether esters such as ethyl or butyl glycol acetate and various ketones.^[16]

Diverging from the solvents described before, a reactive solvent is a solvent that can react chemically with the binder during film formation and remains in the solidifying film. For this reason, they contribute to a reduction in organic emissions.^[16] However, the preferable approach to increase coatings sustainability and reduce VOCs emissions is to use water as the liquid carrier for the composition, i.e., waterborne formulations.^[13] Due to Tintex commitment to sustainability, this is an approach they have opted for, and no coatings are formulated using solvents.

2.2.5 Additives

Additives are substances that are added in small quantities to the coating to improve or modify certain properties of the coating during its manufacture, storage, transportation, or application.^[13] In waterborne coatings, additives have a higher importance than in solvent-based coatings due to the added complexity of formulating in water. The reason for this lies in the fact that water is a strong polar solvent, and therefore has a comparatively high surface tension, resulting in characteristic problems during manufacture and application. Essential additives for stable water-based formulations are surfactants, anti-foaming agents, and rheology-modifying agents.^[18]

Surfactants or emulsifying agents are compounds that reduce the surface tension of a liquid or solid, thus improving the liquid spreading or wetting properties of the system. They consist of amphiphilic molecules, where the hydrophobic end is compatible and orients itself towards the binder, while the hydrophilic end is compatible and orients itself towards the water phase.^[17]

The emulsifiers used in the manufacture of water-based binders are foam-forming substances, and in consequence of the intensive stirring during the coating preparation, it may lead to excessive foaming. The presence of foam creates surface irregularities, reduced

gloss, and transparency, and may decrease the ability of the coating to protect against penetrating media.^[18] Anti-foaming agents are surfactants in the form of tiny droplets or solid particles that enter the foam lamella and destabilize it.^[16]

On the other hand, the application of coatings as foams requires foaming agents and foaming stabilizers in their formulation. Foams are unstable due to various destructive processes such as liquid drainage, bubble coalescence, bubble disproportionation and so on, but they can keep dynamic stability under the action of a foaming agent and a foaming stabilizer, which also lie in the category of surfactants.^[19] The bubble is separated by a thin foam lamella from the surrounding atmosphere and the surfaces of the lamella orientated to the atmosphere and the gas bubble are covered with a surfactant layer.^[18] This process is well demonstrated in Figure 1.

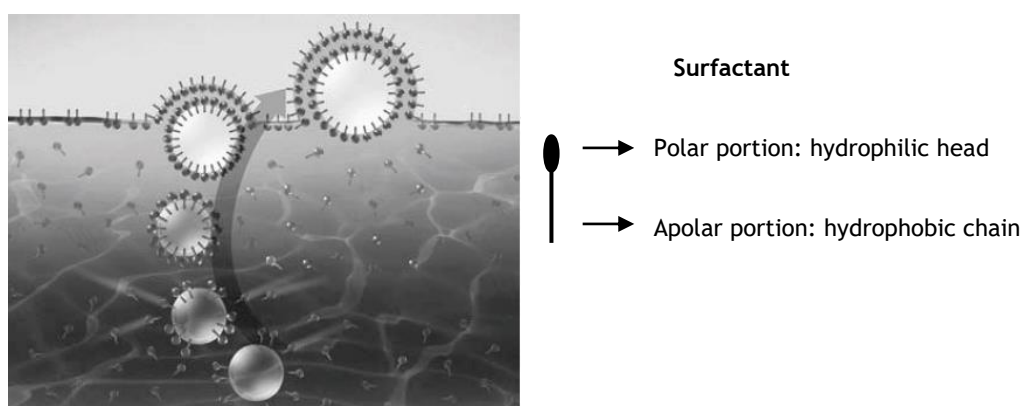


Figure 1 - Formation and stabilization of foam in a liquid. Adapted from [18].

Rheology modifying agents, the so-called thickeners, are added to optimize the flow behavior of the coating by adjusting the viscosity, but also to solve problems related to the state of dispersion of the particles in the formulation.^[13,18] It is possible to distinguish between water phase thickeners (e.g. cellulose and starch derivatives and acrylic thickeners) and associative thickeners (e.g. hydrophobically modified polyoxyethylenes, in particular hydrophobically modified ethoxylated urethanes (HEUR), acrylic thickeners, and cellulose ethers). While water phase thickeners interact predominantly with the water phase, the associative thickeners interact with several components of the coating.^[13] Associative thickeners are water-soluble polymers that feature both hydrophobic and hydrophilic parts, where the hydrophobic segments of the molecule form intermolecular associations with other hydrophobic dispersed particles in the system, forming a net-like structure and thus thickening the liquid.^[20] Water phase thickeners thicken the aqueous phase in two stages: first, the water is bonded through the formation of hydrogen bonds, increasing slightly the viscosity; then, by raising the concentration, it overlaps the polymer chains and increases significantly the viscosity until it reaches the final viscosity of the mixture.^[21]

Since aesthetics is an important parameter of coatings, surface modifiers such as slip additives and matting agents are sometimes added to the formulation. Slip additives provide smoothness, feel and slip ability to the coating surface, while also improving scratch and scrub resistance. In most cases, the coating is formulated to obtain a high gloss, but in many applications a matte surface is preferable. In this case, matting agents can be added to allow a better control of gloss without impairing other properties of the coating.^[14]

In high-performance coatings, it is frequently used catalytically active additives to accelerate the crosslinking reaction and to enhance the other chemical reactions taking place during film formation. Other special effects additives, such as antiskinning agents, light stabilizers, corrosion inhibitors, biocides, flame retardants, and photoinitiators are also frequently used.^[13]

2.3 Waterborne coating formulations

As mentioned before, Tintex coating formulations use water as the liquid carrier for the composition, i.e., waterborne formulations. These are formed by heterophase polymerization in a dispersion medium, for example, by emulsion polymerization. An emulsion is a two-phase liquid system in which small droplets of one liquid are immiscible and dispersed in a second continuous liquid phase.^[22]

Emulsion polymerization starts with the emulsification of hydrophobic monomers by an oil-in-water emulsifier. Then, the reaction initiates with either a water-soluble initiator or an oil-soluble initiator in the presence of a surfactant which may be ionic, non-ionic, or a protective colloid to disperse the hydrophobic monomer through the aqueous solution. The surfactant must be present above the critical micelle concentration to aggregate in the form of spherical micelles and decrease the surface tension. Consequently, the hydrophobic monomers diffuse through the aqueous phase to the micelle and the reaction continues until all monomer droplets are exhausted and the micelle increases in size. The water-soluble initiator enters the micelle where the free radical propagation starts. During this process, monomers diffuse from the solvent droplets through the water phase into the micelle and the polymers grow, while the monomer droplets shrink and gradually disappear. Subsequently, polymers continue to grow until a stable latex is formed. This process is well demonstrated in Figure 2.^[23]

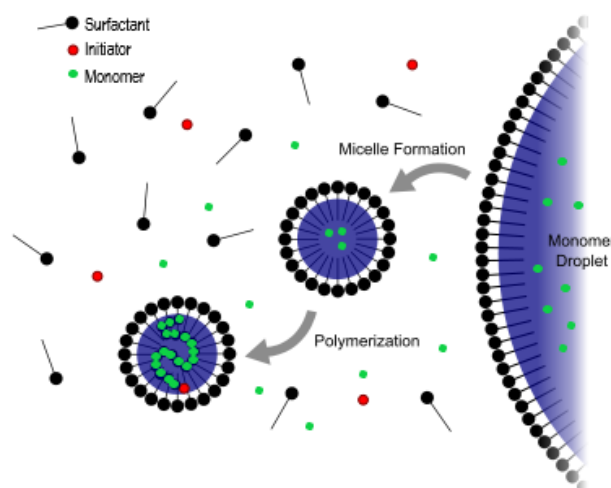


Figure 2 - Schematic representation of emulsion polymerization. Adapted from [23].

2.3.1 Waterborne polyurethane dispersions

Waterborne polyurethane (WBP) dispersions are widely used in waterborne coating formulations. They have gained importance due to their compatibility for usage in VOC-free coatings, fueled by consumer awareness and legislation to reduce VOC emissions. Consequently, their technical quality has seen an increase due to many innovations in basic chemistry, dispersion technology, formulations, and application techniques.^[24]

Polyurethanes main functionality of their backbone is the urethane group (-NHCOO-), formed by the reaction between an isocyanate (-NCO) and a hydroxyl group (-OH). They are block polymers, composed of a soft segment, which consists of the polyol, and a hard segment formed by the isocyanate, and a diol, which is the low molecular weight chain extender.^[25] Polyurethane synthesis is illustrated in Figure 3 below.

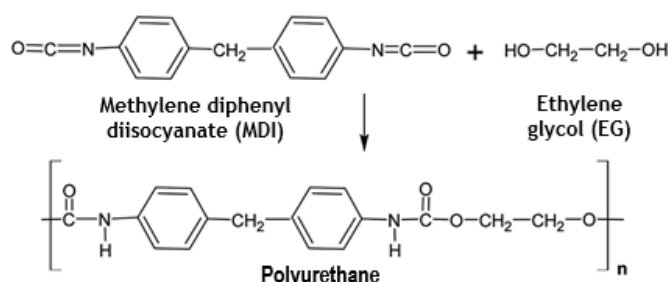


Figure 3 - Reaction between a diisocyanate (MDI) and a polyol (EG) to form polyurethane. Adapted from [26].

The properties of the PUs depend on the polyols and isocyanates from which they were made, so it is necessary to discuss the different types of polyols and isocyanates and their roles in the synthesis process.

Polyols contribute with flexible long segments, which produce soft elastic polymers. They are reactive substances containing at least two isocyanate-reacting groups attached to a single molecule. The different types of polyols used to produce PUs for coatings include:^[26,27]

- Polyesters, such as polycaprolactone polyols, that are prepared by ring-opening polymerization of caprolactone monomer with a glycol. The chemistry is controlled to ensure that these polyols contain terminal hydroxyl groups.
- Polyethers obtained from the reaction between an epoxide and an active hydrogen-containing compound or from ring-opening polymerization of epoxy monomers. One important class of polyether polyol is polytetramethylene ether glycol (PTMEG), used as a reactant in the production of hydrolysis-resistant PU elastomer.
- Amine-terminated polyethers, which are based on polyether polyols, but primary or secondary amino groups substitute the terminal hydroxyl groups.
- Polycarbonates prepared by condensation of phosgene or alkylene glycol carbonates. As in polyesters, the chemistry is controlled to ensure that the polycarbonates contain terminal hydroxyl groups.
- Fluoroethylene vinyl ethers (FEVE) polyols, which are produced from the copolymerization of tetrafluoroethylene or chlorotrifluoroethylene with vinyl ethers containing hydroxyalkyl vinyl ethers.

The isocyanate group is responsible for PU reactivity and curing properties. Isocyanates can be categorized as difunctional or heterofunctional and aromatic or aliphatic. Aromatic isocyanates, such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), are generally cheaper and more reactive than aliphatic isocyanates. Even though aliphatic isocyanates are less used, they find applications in coatings and other areas where transparency and color are sought, since aromatic isocyanate-based PUs usually darken when exposed to light. The most commonly used are isophorone diisocyanate (IPDI), hydrogenated MDI, and 1,6-hexamethylene diisocyanate (HDI).^[26]

The water compatibility of WBPU dispersions can be achieved by adding an internal emulsifier, avoiding the use of organic solvents, which confers environmental advantage. WBPU dispersions also exhibit high solid content and molecular weight, low viscosity, non-flammability properties, and a good film-forming ability at room temperature.^[25]

Traditional methods to synthesize WBPU dispersions include the acetone process and the prepolymer process. The acetone process uses a hydrophilizing diamine (N-(2-aminoethyl)-2-aminoethanesulfonic acid) having a double role of chain extender and internal emulsifier, and the acetone is added to control the viscosity and solubilize the N-(2-aminoethyl)-2-aminoethanesulfonic acid. The prepolymer process was designed as an

alternative to the patented acetone process, providing environmental and economic advantages. An NCO-terminated prepolymer with an approximate molecular weight of $8000 \text{ g}\cdot\text{mol}^{-1}$ is synthesized, formed by the reaction of an isocyanate, a polyol, and an internal emulsifier such as dimethylolpropionic acid (DMPA). Since DMPA is insoluble, a polar co-solvent (e.g. N-Methyl-2-Pyrrolidone (NMP)) is needed. Before the dispersion step, the ionic groups of DMPA are neutralized with a tertiary amine and the viscosity of the system can be adjusted with acetone. During the dispersion step, the prepolymer is dispersed in water and a high molecular weight of the final polymer can be achieved through a chain extension reaction with di- or polyamines in a heterogeneous medium. However, the use of solvents present hazards to the environment and solvent-free aqueous polyurethane dispersions formed by prepolymer processes have gained more importance recently. The synthesis route is as follows: the NCO-terminated hydrophilic prepolymer is obtained by reaction of long-chain diols and hydrophilic dihydroxyl compounds with excessive diisocyanate in the absence of solvent. The prepolymer disperses in water under high-speed agitation, and the chain extension is completed by adding diamines into the water-based prepolymer dispersion.^[25,28]

2.3.2 Waterborne acrylic dispersions

Waterborne acrylic dispersions are well-known as binders in the production of coatings. Acrylic resins, also known as acrylates or polyacrylates, are synthesized by acrylate or methacrylate as the main monomers by radical-initiated chain-growth polymerization (Figure 4).^[14]

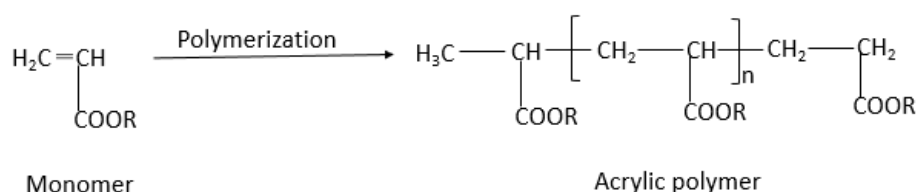


Figure 4 - Polymerization reaction for acrylic resins. Adapted from [14].

Besides methacrylate monomers, non-acrylate monomers (typically vinyl monomers) are also used in the production of commercial acrylic polymers resins to impart reactive functionality or lower cost. This wide variety of possible monomers allows the manufacturers to customize these resins accordingly to the requirements of the end product. Acrylic resins exhibit strong light, heat, and chemical stability, therefore, the coating prepared by it presents weather resistance, pollution resistance, as well as acid and alkali resistance, and a low cost.^[14,29]

As seen for WBPU dispersions, acrylic dispersions have been widely used due to being compliant with VOC-free coatings. Moreover, unlike solvent-based polymer solutions, the viscosity of polymer dispersions is not dependent on the molecular weight of the polymer particles, allowing formulators to use very high molecular weight acrylic resins. Waterborne acrylic dispersions are high molecular weight acrylic (co)polymer particles dispersed in water, prepared by radical polymerization mechanism via emulsion polymerization, which has been explained priorly.^[14]

2.4 Substrate and coating interactions

The nature and structure of the substrate have a great impact on the outcome of the coating process, since it is the structure that defines the morphological profile of the coating deposition and the final thickness of its layer, hence contributing to the ergonomics, durability, elasticity, and water and air permeability of the final product. For this reason, understanding the coating/substrate interactions is of critical importance in order to design a product that fulfills the end-use requirements.

Fibers are long, fine forms of matter with diameters of the order of ten micrometers and lengths ranging from a few millimeters to virtually being continuous. A fiber is the most basic unit of clothing and it is the elemental point to envision different styles and patterns. They can be distinguished as natural fibers, both those obtained from plants (e.g. cotton) and animals (e.g. wool and silk), organic synthetic fibers (e.g. polyester), including regenerated cellulosic viscose rayon, and inorganic fibers, such as glass, carbon, and ceramic fibers. Cotton has been the most commonly used textile substrate for coating for a long time, but synthetic fibers are becoming more predominant due to their strength and easy processing.^[10,30,31] At Tintex, the most used fibers are cotton, polyester, lyocell (a form of rayon), spandex, and polyamide.

In Figure 5, it is represented the three basic types of textile structures: woven, weft-knitted, and warp-knitted textile fabric. Weaving is the intersection of two sets of straight yarns, warp and weft, which cross and interlace at right angles to each other, to produce woven fabrics. The warp is the yarn going across the length of the loom, whilst the weft is the yarn going across the width of the fabric. In the weft-knitted production, a single yarn bobbin is used to form loops (held by needles) into which new loops of the same yarn can be formed and the yarn is led from side to side in flat-knitting and circularly upwards in circular knitting. This type of fabric tends to show deformation which makes it easy to fit onto a human body. The four primary structures that are base structures from which all weft-knitted fabrics are derived are jersey, rib, purl, and interlock. Tintex fabrics are mostly jersey and interlock

structures. The jersey is produced by the needles knitting as a single set, drawing the loops away from the technical back and towards the technical face side of the fabric. The interlock was originally derived from rib but requires a special arrangement of needles knitting back-to-back in an alternate sequence of two sets, so that the two courses of loops show wales of face loops on each side of the fabric exactly in line with each other, thus hiding the appearance of the reverse loops. Regarding the warp-knitted fabric, it is an intermediate between weaving and weft knitting, where the yarns are vertically placed side-by-side, similar to the warp yarns in weaving and placed in guiders in order to allow them to be interlocked with each other horizontally. It typically shows better mechanical properties than the other textile structures, making it ideal for many high-tech applications.^[10,32]

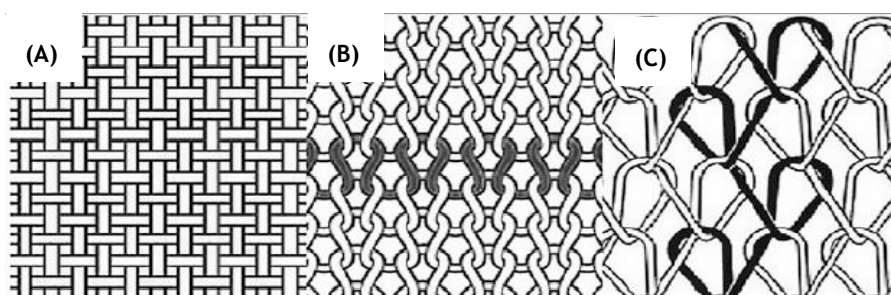


Figure 5 - Illustration of textile fabrics: (A) woven structure, (B) weft-knitted structure, (C) warp-knitted structure. Adapted from [10].

Two important factors to consider when discussing the coating and substrate interactions are the wetting of the fabric by the coating material and the adhesion of the coating to the fabric. Adhesion is the attraction between two materials in contact and is determined by the intermolecular forces between the two materials. In most textile coating processes these forces are polar or dispersive. If the two materials present a high molecular affinity it will generate a low energy interface and high work of adhesion, i.e., high energy required to separate two layers in contact, thus leading to a good adhesion. Another factor contributing to a good adhesion is the interfacial diffusion of polymer chains since when a material is heated above its glass transition temperature, the polymer chains achieve greater mobility and can penetrate deeper by diffusion. Wetting can be defined as the displacement of a fluid from a solid surface by a second immiscible fluid, where the first fluid is usually air and the second is the fluid used in the coating process. Considering that the physical materials are fabric (solid), coating (liquid), and air (gas or vapor), when the coating is applied to the fabric three interfaces are formed: a solid-liquid interface, a solid-vapor interface, and a liquid-vapor interface. According to Thomas Young, since the energy of a system must be at a minimum at thermodynamic equilibrium, the only mobile interface is the liquid-vapor interface, which means that the shape of the liquid droplet will be variable. At equilibrium, the angle between the liquid-air and solid-air interfaces reaches a certain value,

the contact angle θ , as demonstrated in Figure 6. The contact angle is given by Equation 1, proposed by Thomas Young:

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos \theta \quad (1)$$

where γ_S is the interfacial tension between solid and vapor, γ_{SL} is the interfacial tension between solid and liquid, and γ_L is the interfacial tension between liquid and vapor.^[7,33]

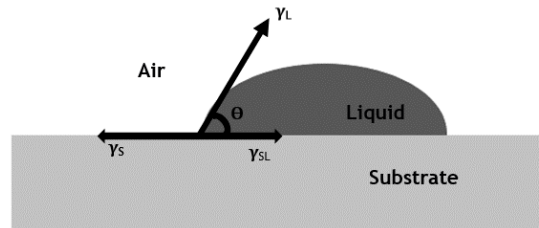


Figure 6 - Representation of the interfacial tensions and contact angle of the coating system. Adapted from [33].

The contact angle measures a material's wettability by the wetting media, in the sense that the lower the contact angle, the higher wettability. The substrate surface has an impact on the contact angle of the coating because textile substrates are rough and porous, so penetration through the fibrous structures may occur. Figure 7 shows an example of poor and good wettability. In the case of Figure 7(A), the coverage of the coating is spotty and does not penetrate, which means the contact area is smaller than the geometrical area, thus leading to weak adhesion. Figure 7(B) shows the case of a good wettability of the surface and the contact angle approaches zero degrees. In this case, there is full coverage, and the coating starts to wrap around the individual fibers and fill in the interstitial spaces, maximizing the adhesion.

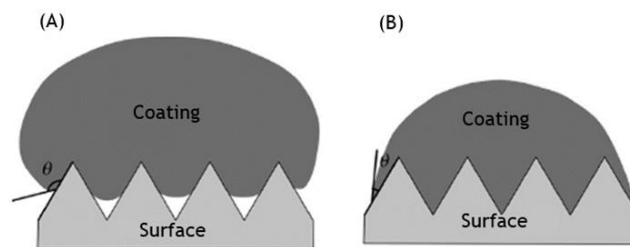


Figure 7 - Coating/textile surface coverage having a (A) poor wettability and (B) good wettability. Adapted from [33].

2.5 Coating methods

The most implemented coating methods and technologies in the industry are dip coating, knife or blade coating, air-knife coating, screen printing, and spray coating. At Tintex, the two types of technologies installed at an industrial scale are the knife-over-roller and rotary screen printing.

The knife-over-roller technique consists of applying the coating material in excess in the substrate, and a knife or blade suspended above a roller is used to spread the coating material. The roller can be made of steel or rubber. There is a gap between the substrate and the knife, which controls the thickness of the coating. The gap height, blade angle, coating speed, and the shear viscosity of the formulation are the parameters that influence the degree of penetration and consequently, the degree of adhesion.^[10,33] This method is represented in Figure 8 below.

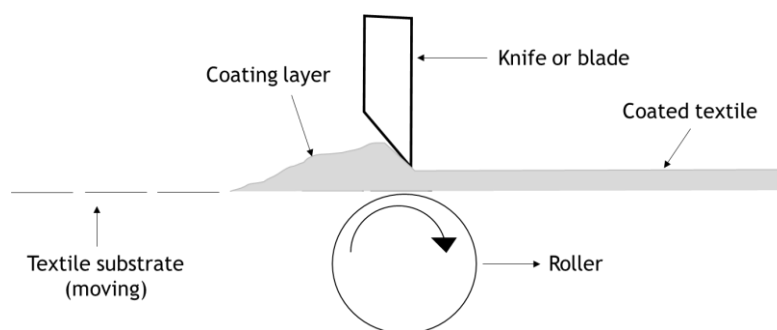


Figure 8 - Schematic representation of knife-over-roller coating. Adapted from [10].

The basic principle behind screen printing is that the printing formulation is pressed through a screen onto the textile substrate. Rotary screen coating contains a screen that is a seamless nickel cylinder with perforations. The fabric usually rests on a rubber mat that moves the fabric forward under the rotating screen. A squeegee is placed over the screen, used as the supply and distribution pipe of the coating formulation, by squeezing out the coating through the perforations of the screen, coming out in the form of dots that merge together to form a continuous coating. In addition, a backup roll is used for counterpressure. In this process, the screen, the rubber mat, and the counterpressure roll all move at the same speed, resulting in a coating that is done without friction and tension. For this reason, this method is suitable for delicate and stretchable fabrics. The amount of coating applied is controlled by the mesh number of the screen, the squeegee pressure, and the viscosity of the coating formulation.^[10,34] A scheme of the rotary screen coating is represented in Figure 9.

But before the industrial application of the coating, multiple samples are prepared at lab scale resorting to knife or blade coating techniques, to achieve the desired coating

properties. These samples are then submitted for quality control tests and only then can be produced at a larger scale.

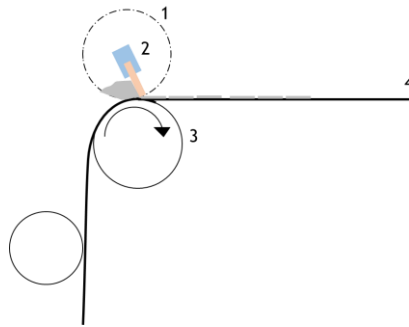


Figure 9 - Schematic representation of rotary screen coating: (1) Screen, (2) Squeegee, (3) Counterpressure roll, (4) Rubber mat. Adapted from [34].

The last step of the process involves complementary processes of finishing of the morphology of each layer. For this step, Tintex utilizes calendering or embossing equipment.

The calender consists of a set of high-pressure cylindrical rolls nipped together under mechanical load and driven via a system motor. The rolls can be heated or chilled as needed to keep the coating malleable or release the coating, respectively. It can be used to improve the surface finish, for improved aesthetics, to reduce product thickness, to densify the coating, and so on. The coating to be calendered is placed in contact with a polished surface of a steel hot roll and passes through the roll nips. The nip area, as shown in Figure 10, is the physical contact between the hot roll and a compliant roll.^[7,34,35]

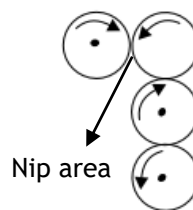


Figure 10 - Configuration of the calender rolls. Adapted from [34].

Embossing is a method to provide the coating with a desired pattern by using a printing paper pressing against a backup roll under controlled conditions of pressure, temperature, and pressing time.^[36] At Tintex, the embossing machine is used, for example, to give a leather-like handle to the coatings.

2.6 bluesign® label

The idea of the bluesign® system started from a project initiative in 1997, in Switzerland, in a collaboration with a textile company (Schoeller Textil), a retailer company

(Nike), and a chemical company (Huntsman), as an effort to develop a textile product with the lowest possible environmental impact, resource-improving production and augmented safety for workers and consumers. To make this system available to many textile companies as possible, an independent company, Bluesign Technologies AG, was founded in 2000, in Switzerland.^[6,37]

Bluesign is based on five principles that its partners must fulfill:^[37]

- Resource productivity - the aim is to produce textiles using as few resources as possible, leading to a reduction in the environmental impact, and therefore to a product with an added value.
- Consumer safety - manufacturers should be able to meet the consumer requirements of a high-quality product without health risks and an associated production process with sustainability implemented in every step.
- Minimum aquatic environment impact - the objective is to minimize the amount of water used and harmful substances that contaminate wastewater. Effective ways include the selection of sustainable process components, optimization of the production, and the installation of wastewater treatment technology.
- Reduced CO₂ emissions - the aim is to reduce CO₂ emissions within the company's sphere of influence, as well as during the subsequent processes, by a strict selection of raw materials and chemical products according to their emission impact, and cleansing and recycling of the exhaust air.
- Occupational Health and Safety - the health and safety of the employees must be safeguarded by strict labor norms, including safety measures and protection against environmental pollution, such as dust and noise.

bluesign® has a rating system for each applied chemical component that is described in Figure 11 below. The Bluesign Finder consists of a web-based, advanced search engine for manufacturers that contains all bluesign® approved chemicals that meet bluesign® criteria and important information needed to utilize these products in compliance with the bluesign® system. BSBL stands for Bluesign System Black Limits which is a compilation of substances with carcinogenic, mutagenic, or reprotoxic properties, or those falling under the Persistent Organic Pollutants regulation.^[6]

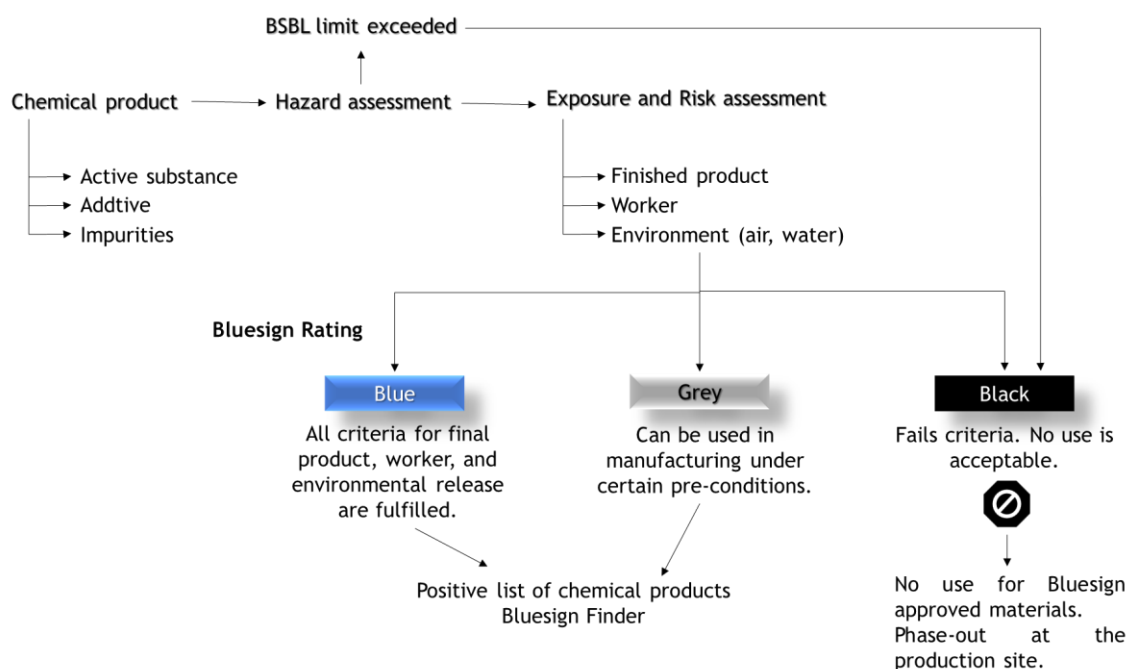


Figure 11 - Rating criteria of the bluesign® system. Adapted from [6].

In order to have a bluesign® certified product, these are the steps a company like Tintex must fulfill:

1. Define the usage range of the product - usage ranges classify consumer goods according to their consumer safety relevance, with A being the most stringent category:
 - Usage range A: Next to skin use and baby articles (0 to 3 years).
 - Usage range B: Occasional skin contact.
 - Usage range C: No skin contact.
2. Validate the consumer safety limits and usage restrictions:
 - pH: Acceptable ranges are 4 to 7.5 for non-leather products, and 3.5 to 7.5 for leather products.
 - Odor: No unpleasant odor shall be emitted from the products.
 - Sensitizing disperse dyes: Disperse dyes that are sensitizing and classified with the risk phrase R 43/H 317 are not allowed for the usage range A.
 - Textiles dyed with disperse or metal complex dyes: For textiles dyed with disperse or metal complex dyes, fastness to perspiration must be at least between 3 and 4.
 - Color fastness to saliva and perspiration: Colors must be fast to saliva and perspiration in articles with potential risk for mouthing and/or exposure to babies.
 - Restrictions and bans for chemical substances.
3. Send a sample of the product to bluesign® to finalize the certification process.

The increasing pressure on brands, and consequently manufacturers, to implement strong sustainability policies and guarantee the highest level of transparency and traceability, led to an increased importance of eco-labels in textile products. This triggered a rapid growth of the bluesign® company, and its system has been adopted by worldwide leading textile and accessory manufacturers, such as Patagonia, North Face, and Norway's Helly Hansen. Recently, Tintex Textiles, S.A. has also become a partner of the bluesign® system.^[6] Nowadays, it is considered the biggest sustainability label in the textile industry. Recent important achievements include being recognized by the German government as a credible measure of sustainable manufacturing for public procurement purposes^[38] and supporting Amazon's Climate Pledge Friendly, making it easier for customers to shop for sustainable products.^[39]

Recent research on bluesign® approved textile coatings relies on developing coatings with alternative polymers to side-chain fluorinated polymers, which are mostly used in low surface energy applications and may degrade into per- and polyfluoroalkyl substances (PFAS), and long-chain PFAS. PFAS are prohibited by bluesign®, as fluorine-bearing monomers can cause human health problems in textile processing. Some alternatives include polymers sourced from renewable resources, such as carbon dioxide, terpene, vegetable oil, lignin, and cellulose, as well as waterborne polyurethane and water-based polyurethane with acrylate terminal group.^[5,40]

3 Materials and Methods

3.1 Materials

In an initial phase, it was made a selection of coating compounds of Tintex supply that were validated by Bluesign Finder. This selection was made based on the technical and safety data sheets of each compound to know which ones were compatible with each other, and having in mind the compounds that presented the most promising characteristics.

In this initial phase, the coating formulation was developed to be applied both as a paste and stable foam in pre-qualifying tests to intend if any problems occurred during the mixing phase and after drying (e.g. cracking) in both states. As mentioned before, a usual stable foam formulation would require foaming agents but there was none available in Tintex supply of bluesign® approved coating compounds. As an alternative, water was added to help in the foaming creation. Due to the low pH of Edolan AM compared with the other compounds, it is necessary to add ammonia in order to maintain a steady pH under neutral to slightly alkaline conditions to stabilize the coating formulation.^[41]

Even though a paste formulation does not usually need foam stabilizers, their surfactant nature is required in waterborne formulations to help stabilize the emulsion, hence they can be used in both paste and stable foam formulations. Water is also needed in both cases because besides helping in the foaming creation, it also maintains the viscosity of the blend as desired.

In the final phase, after concluding that the coating applied as a paste had the best technical functionality, the coating formulation was improved. The selected coating compounds selected in the initial phase and for the improved formulation are described in Table 2. Their pH, solid content, mass fraction, and function are discriminated in Table 3.

Some characteristics of the substrates used in the pre-qualifying tests are shown in Table 4. For quality control tests it was only used the interlock cotton with the higher grammage and interlock polyester knits.

3.2 Methods

3.2.1 Preparation of the coating samples

All the equipment used during the preparation of the coating samples is listed in Appendix B. The method to prepare the coating samples at Tintex is described as follows.

Table 2 - Coating compounds selected in the initial phase and in the formulation improvement

Commercial name	Chemical basis	Supplier
Impranil eco DLS	Aliphatic polyester-polyurethane dispersion	Covestro
Edolan AM	Dispersion of an acrylic polymer	Tanatex Chemicals
Impranil DL 2077	Polyurethane dispersion	Covestro
Tubicoat SHM	Aqueous solution of ammonium stearate	CHT
Tubicoat stabilisator RP	Alkyl sulphosuccinamide	CHT
Arkophob DAN New liq	Polyurethane dispersion	Archroma
Luprintol Emulsifier PE New	Non-ionic surfactant in water	Archroma
Appretan Thickener 2710 Liquid	Polyacrylic acid derivative	Clariant
Ammonia solution 25%	-	Quimitejo
Water	-	-
Antimussol SFE liquid	Hydrocarbons with emulsifiers	Clariant
Nuva N2155 liq.	Dispersion of a fluorine compound	Clariant

Table 3 - Characteristics of the selected coating compounds

Commercial name	Function	pH	Solid content (%)	Mass fraction (%)	
				Initial phase	Improved formulation
Impranil eco DLS	Binder	7.5	50	34.93	33.40
Edolan AM	Binder	3.0 - 6.0	49	19.96	19.08
Impranil DL 2077	Binder	7.5 - 9.5	35	9.98	9.54
Tubicoat SHM	Foam stabilizer	~10.0	*	3.99	0.95
Tubicoat stabilisator RP	Foam stabilizer	9.0 - 10.0	34	1.49	1.91
Arkophob DAN New liq	Crosslinker	*	*	6.99	6.68
Luprintol Emulsifier PE	Emulsifier	~7.0	*	1.00	0.95
Appretan Thickener 2710 Liquid	Thickener	8.0 - 9.0	*	1.20	1.25
Ammonia solution 25%	pH stabilizer	11.0 - 12.0	*	0.50	0.48
Water	Foaming agent	~7.0	*	19.96	9.54
Antimussol SFE liquid	Anti-foaming agent	~7.0	*	-	6.68
Nuva N2155 liq.	Hydrophobic agent	~4.5	*	-	9.54

* This information is not mentioned either in the technical or safety data sheets.

Table 4 - Characteristics of the substrates used in the pre-qualifying tests

Fiber	Grammage (g·m ⁻²)	Structure
Cotton	150	Jersey
Cotton	410	Interlock
Cotton	245	Interlock
Polyester	140	Interlock

First, all the ingredients, except the thickener, are weighted in a 1 L plastic beaker with a precision balance (± 0.01 g) (METTLER TOLEDO) to obtain a mixture with 200 g according to the mass fractions described in Table 3. Then, the mixture starts to be homogenized in a mechanical stirrer with a 4-bladed propeller stirrer (IKA EUROSTAR 20 digital), at 150 RPM. At first, the amount of thickener is not specified in the formulation and it is added in small quantities at the homogenization step at 250 RPM to dissolve any lumps. It is necessary to visually analyze the presence of excess air bubbles and if so, reduce the rotational speed to ensure that poor foaming does not occur. As the viscosity of the mixture starts to increase, the rotational speed is increased gradually up to 750 RPM. All the ingredients are left to interact until the mixture is completely homogenized and the viscosity of the blend is within the range desired. If the viscosity is still lower than the required, another small amount of thickener is added to the mixture. At the end of this step, the dynamic viscosity is measured with a rotational viscometer (Thermo Scientific HAAKE Viscotester 2 Plus) after calibrating the equipment, at a temperature of approximately 25 °C.

If the application is going to be a stable foam the next step is to incorporate air into the mixture with the help of an electric hand mixer (Bosch). This process ends when the appearance of foam is visually identifiable and soft peaks are formed. It is now necessary to determine the foam density, as it is an important parameter to characterize the coating formulation. A stainless steel cup is filled with the foam and weighted in the precision balance. Since the mass and volume of the cup can be previously known, the foam density can be obtained from Equation 2:

$$\text{Foam density} = \frac{m_{\text{cup+foam}} - m_{\text{cup}}}{V_{\text{cup}}} \quad (2)$$

where $m_{\text{cup+foam}}$ represents the mass of the cup filled with the foam (g), m_{cup} is the mass of the cup (g), and V_{cup} is the volume of the cup (L).

The next step is to apply the coating onto the substrate. At lab scale, Tintex utilizes a Werner Mathis Lab Coater&Dryer to apply the coating resorting to the knife-over-roller

method. After the knit is set, the gap between the knit and the knife is controlled according to the thickness that is defined for each application. The stable foam was applied with a thickness of 0.5 mm and the paste was applied both with a thickness of 0.1 and 0.5 mm. The gap is measured with a feeler gauge (Teng FG20100). The coating is then applied in excess in the substrate and is evenly distributed by the substrate as the knife moves forward. The coating is now ready to be dried, followed by a complementary process of finishing in the Monti Antonio roll calender model 93-2000sp, and finally polymerized. The application conditions for both the paste and the stable foam are specified in Table 5. In the end, the thickness of the coated knit after being dried, calendered, and polymerized, was measured with an outside micrometer (MIB-Messzeuge).

Table 5 - Drying, calendering, and polymerization conditions of the stable foam and paste

	Drying		Calendering		Polymerization	
	Stable foam	Paste	Stable foam	Paste	Stable foam	Paste
Temperature (°C)	80 to 100	80 to 100	90	90	150 to 170	150 to 170
Dwell time (min)	4	4	-	-	4	4
Rotational aeration speed (RPM)	1000	1000	-	-	1300	1300
Pressure (bar)	-	-	120	150	-	-
Velocity (m·min ⁻¹)	-	-	3	3	-	-

For the sake of practicality, the samples were given a code accordingly to the state of the application (paste or stable foam), the thickness of application, and the substrate used, as indicated in Table 6. CO INT stands for cotton interlock and PES INT for polyester interlock.

Table 6 - Codes attributed to each sample

State of the application	Thickness of application (mm)	Substrate used	Code
Paste	0.1	CO INT	CO_0.1
Paste	0.5	CO INT	CO_0.5
Stable foam	0.5	CO INT	CO_FOAM
Paste	0.1	PES INT	PES_0.1
Paste	0.5	PES INT	PES_0.5
Stable foam	0.5	PES INT	PES_FOAM

3.2.2 Quality control tests

After the pre-qualifying tests, the second phase was the realization of quality control tests at Tintex to select the sample that presented the most promising characteristics and further optimize the formulation or the processing conditions if necessary. Of the pre-qualifying tests, the jersey cotton knit was discarded for this phase, since Tintex prefers the interlock structure for coatings because it presents higher dimensional stability and flexibility than the jersey structure. The selected knits for these tests were the interlock cotton with $410 \text{ g}\cdot\text{m}^{-2}$ of grammage and the polyester. The quality control tests performed are described below.

The **Pilling Box test** was performed employing the NP EN ISO 12945-1 standard. It consisted of mounting four samples on polyurethane tubes and, after cleaning the pilling box (James Heal) (Figure B-8), which consists of a cork-lined cubical box, the samples were placed inside the box, the instrument was started, and the samples were tumbled and rubbed with the cork material. After 11000 cycles, the samples were taken out and compared with the original sample to evaluate the formation of pilling.

The **Martindale pilling test**, according to the NP EN ISO 12945-2 standard, was carried out in a Martindale machine (James Heal) where circular samples were placed in the lower plates of the machine and rubbed under load against itself, performing a Lissajous pattern. At the end of 8000 rubs, the amount of fuzz was assessed. The **abrasion test** (NP EN ISO 12947-2) is very similar to the aforementioned but instead of the circular sample rubbing against itself, it rubs against a wool standard fabric. After 2000 cycles, the sample was inspected for wear and tear traces. The Martindale machine is illustrated in Figure 12(A).

The **dry and wet rubbing color fastness** was tested in a crockmeter (James Heal) using the NP EN ISO 105-X12 standard. This equipment is utilized for testing the transference of shading from the surface of one material to another by either wet or dry rubbing, but it can also be employed to perform rub abrasion tests. The sample was placed on the base of the crockmeter and held in place with the sample holder. The rubbing action was provided by an acrylic “finger” involved with either a dry or wet standard white cotton cloth, which moved back and forth in a straight line, to make the sample and the white cotton rub each other. After ten reciprocating movements, the degree of color adhesion on the white cotton cloth and the stability of the coating surface were evaluated with the help of a gray scale and under appropriate lighting. The crockmeter is illustrated in Figure B-9.

The **wash resistance test** was performed in a domestic washing machine, at 30°C with a small amount of a detergent with a specific formulation to be used for testing purposes, in a wash cycle of 30 min. After completing ten washing cycles, the sample was compared with the original sample to assess if there was any difference in the coating surface.

The **resistance to water penetration test** measures the hydrostatic head supported by a fabric, which is a measure of the opposition to the passage of water through the fabric. This test was performed in a TEXTEST Automatic Hydrostatic Head Tester FX 3000 HydroTester IV (Figure 12(B)). The testing head was filled with distilled water and the sample was placed with the face, i.e., the side of the fabric in which the coating is applied, in contact with the water. The test area was 100 cm² and the rate of increase of the water pressure was 10 mbar H₂O·min⁻¹. The test ended when water penetration occurred in three places and the pressure at that moment was noted.

Water repellency describes the resistance of the fabric to surface wetting and water penetration. This test was performed employing the AATCC test method 22, using a spray tester (James Heal), where 250 mL of distilled water was poured into a funnel, which was sprayed to the sample that was placed in a holder. After the spray ceased, the sample was tapped against a solid object, and finally, the spray rating was determined by comparing the appearance of the sample with descriptive standards and photographs. The spray tester is illustrated in Figure B-10.

In the **air permeability test**, the rate of airflow passing perpendicularly through a known area of fabric is adjusted to obtain a prescribed air pressure differential between the two fabric surfaces. From this rate of airflow, the air permeability of the fabric is determined. This test was performed in a TEXTEST Air Permeability Tester FX 3300 LabAir IV (Figure B-11), employing the NP EN ISO 9237:1997, using a test area of 20 cm² and a pressure of 100 Pa.

In order to know if this product was eligible for the bluesign® label, it was necessary to determine the pH of the aqueous extract of the textile following the ISO 3071 standard guidelines. Each test specimen and 100 mL of the extracting solution (potassium chloride solution) were placed in a stoppered flask and mechanically stirred for 2 h ± 5 min. A portion of the extract was then decanted into a beaker and the pH was measured by immersing the electrode of the pH-meter in the solution.

3.2.3 Chemical, mechanical and morphological characterization

The third phase consisted of the realization of more fundamental tests at FEUP for the chemical, mechanical and morphological characterization of the CO_0.5 and PES_0.5 samples. The chemical and morphological characterizations were done through SEM (Scanning Electron Microscopy), FTIR-ATR (Fourier Transform Infrared - Attenuated Total Reflectance), Raman spectroscopy, DSC (Differential Scanning Calorimetry), and TGA (Thermogravimetric analysis). The mechanical characterization was done resorting to the grab test method to determine the breaking strength.



Figure 12 - Quality control equipment: (A) Nu-Martindale Abrasion and Pilling tester; (B) Automatic Hydrostatic Head Tester FX 3000 HydroTester IV.

SEM images were taken using a Phenom XL scanning electron microscope (Thermo Fisher Scientific), operating at a voltage of 15 kV. The samples examined were the CO_0.5 and PES_0.5 samples, the raw (i.e., the knits without any type of treatment and finishing), the treated cotton and polyester knits, a sample previously developed by Tintex, and a sample of the improved formulation applied on the cotton knit. The equipment is illustrated in Figure B-12.

The FTIR-ATR absorbance spectra were obtained from a VERTEX 70 FTIR spectrophotometer (BRUCKER) (Figure 13(A)) with a high-sensitivity DLaTGS detector at room temperature and an A225/Q PLATINUM ATR diamond crystal. The specifications of the spectrophotometer were set at 4 cm^{-1} resolution with an average of 64 scans in the scanning range of $500\text{--}4000\text{ cm}^{-1}$. The normalized second-order derivative of the spectra was employed by selecting 17 smoothing points and choosing the Savitzky-Golay (SG) quadratic/cubic numerical algorithm as the smoothing method. The samples analyzed were the CO_0.1 and CO_0.5 samples, the PES_0.1 and PES_0.5 samples, the raw and treated cotton and polyester knits, and the coating by itself (not linked to any substrate). The coated samples were examined two times, in two different zones, to infer if the spectrum was the same along the coating surface. The knits and the sample of the coating by itself were examined only one time in one zone.

The Raman spectroscopic measurements were obtained using a WITec Alpha300 R Micro-Raman (Figure 13 (B)), and the data were treated by WiTec software. A laser with a wavelength of 532 nm was used as an excitation source. All spectra from the samples were acquired in the spectral range between 3800 and 500 cm^{-1} , with 60 accumulation points and an integration time of one second. The confocal Raman images were obtained with an integration time of 0.50 s per spectrum, in a scan range of $800\times 800\text{ }\mu\text{m}^2$ and $400\times 100\text{ }\mu\text{m}^2$ for

the color-coded Raman images and depth-profiling images, respectively. The samples analyzed were the CO_0.5 and PES_0.5 samples.

The thermal measurements (calorimetric analysis and thermogravimetric analysis) were performed in the CO_0.5 and PES_0.5 samples, and a sample of the coating by itself. DSC measurements of the samples were carried out using a DSC 14 Polyma (NETZSCH) calorimeter (Figure B-13). The samples were heated from -30 °C up to 280 °C at a rate of 10 K·min⁻¹ in a nitrogen atmosphere, which was pumped at 40 mL·min⁻¹. Each sample, weighing between 5 and 15 mg, was weighted in a concave aluminum pan, which was then sealed with a pierced lid. TGA measurements of the samples were performed on an STA 449 F3 Jupiter (NETZSCH) thermo analyzer (Figure B-14). In each case, a 10 to 15 mg sample was examined under a nitrogen atmosphere at a flow rate of 30 mL·min⁻¹. The heating rate was 10 K·min⁻¹ from 30 °C to 600 °C.

The transversal and longitudinal breaking strengths of the CO_0.5 and PES_0.5 samples, as well as the uncoated treated cotton and polyester knits, were tested using a universal testing machine (Tinius Olsen H50KT) at Polytechnic Institute of Viseu and employing the ASTM D 751-06 standard. The grab test was performed at a gauge length of 75 mm and a crosshead speed of 5 mm·s⁻¹.

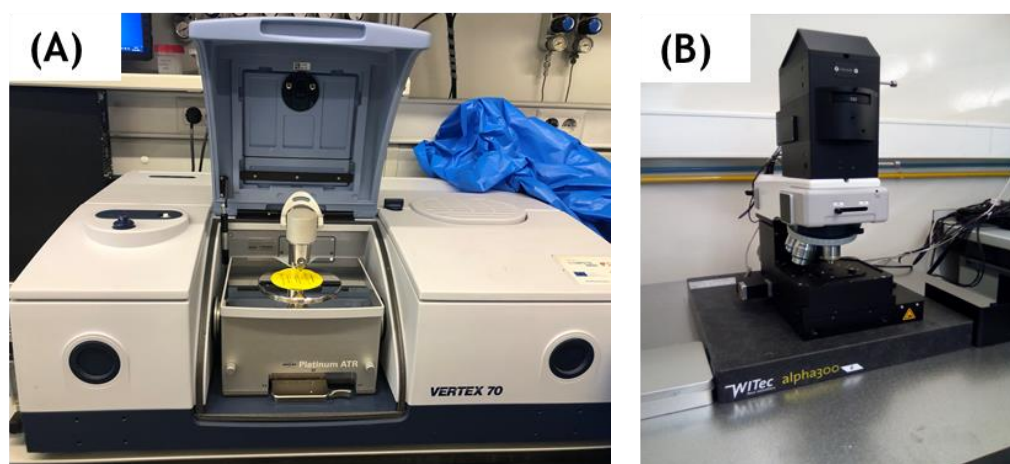


Figure 13 - Chemical characterization equipment: (A) VERTEX 70 FTIR spectrophotometer; (B) WITec Alpha300 R Micro-Raman.

4 Results and discussion

4.1 Pre-qualifying tests

As mentioned before, the pre-qualifying tests served to verify the existence of any problem during the mixing of the compounds or after drying and polymerization. But in addition to that, they also made it possible to infer the repeatability of the formulation and the application process, and whether the final result was visually appealing or not.

The average viscosity of the blend (number of trials (n) = 16) is 48.35 ± 7.15 dPa·s with a coefficient of variation (CV) of 15%. The foam density (n = 12) averaged 311.83 ± 15.28 g·L⁻¹ with a CV of 5%. The coefficient of variation is below 30% for both viscosity and foam density, which suggests that the formulation has repeatability.^[42]

Another relevant measured parameter is the thickness of the coated knit. Knowing the thickness of the knit, it is possible to determine the thickness of the coating in the final conditions (at the surface) and compare it with its application thickness. The values of the measured coated knit thicknesses shown in Table 7 are the mean of 6 trials of each sample and they all show a CV significantly below 30%, suggesting once more repeatability of the formulation and the application process. From Table 7 it can be seen that the final coating thickness is lower in the cotton knit than in the polyester knit (except for the stable foam), probably due to different structures of the substrates. The polyester threads tend to be more compact, making it more difficult for the coating to fill in the interstitial spaces, depositing more over the knit surface.

Table 7 - Determination of the coating thickness in the final conditions

Sample	Thickness of application (mm)	Coated knit thickness (mm)	CV (%)	Knit thickness (mm)	Coating thickness in the final conditions (mm)
CO_0.1	0.10	0.51*	*	0.51	<0.01
CO_0.5	0.50	0.60 ± 0.01	1.28	0.51	0.09
CO_FOAM	0.50	0.59 ± 0.03	4.99	0.51	0.08
PES_0.1	0.10	0.29 ± 0.01	1.75	0.25	0.04
PES_0.5	0.50	0.38 ± 0.01	3.96	0.25	0.13
PES_FOAM	0.50	0.30 ± 0.01	1.92	0.25	0.05

*Given the precision of the outside micrometer (± 0.01 mm) it was not possible to determine the standard deviation and CV.

Visually, no problems occurred neither on the mixing process nor during the processing of the coated knit (drying, calendering, and polymerization), since no cracks were formed. Figure 14 shows one of the samples in the final conditions. As it can be seen, the coating appears to be almost transparent, which is a quality often desired in the textile coating industry. To conclude about the transparency of the coating, it was applied as a paste with 0.5 mm of thickness to a blue cotton knit with $245 \text{ g}\cdot\text{m}^{-2}$ of grammage (Figure 15). Even though it is not completely transparent, it gives this illusion, which is an asset to consider when developing a product.

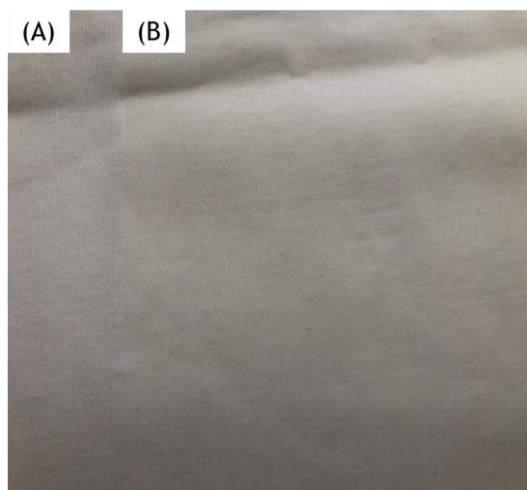


Figure 14 - CO_0.5 sample, where (A) is the uncoated part and (B) is the coated part.

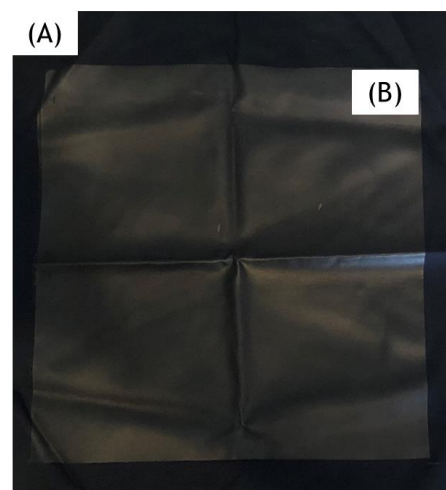


Figure 15 - Coating applied on a blue knit, where (A) is the uncoated part and (B) is the coated part.

4.2 Quality control tests

The results obtained in the Martindale abrasion, dry and wet rubbing color fastness, Pilling Box, Martindale pilling, and wash resistance tests are presented in Table 8. These results were evaluated on a scale of 1-5, where 1 means very unsatisfactory and 5 means very satisfactory. The results are very similar between the cotton and the polyester samples, with ratings ranging from 4 to 5, except for the wash resistance test, where the polyester samples were better (rating 4 compared to 3-4 for cotton), which can be explained by the fact that polyester fibers are less prone to shrinkage and hold onto colors much better.^[43] Nevertheless, this is not a significant difference and overall all the samples presented satisfactory results, even when compared with other Tintex products, so there was no need to change the formulation or the processing conditions at this phase.

When developing a new textile product, some of the most demanded tests are the resistance to water penetration, water repellency, and air permeability, because these give technical information that describes the functional performance of products.

Table 8 - Rating of the quality control tests on a scale of 1-5

Sample	Martindale abrasion test	Dry and wet rubbing color fastness test	Pilling Box test	Martindale pilling test	Wash resistance test
CO_0.1	4	5	4	4	3-4
CO_0.5	4	5	4	4	3-4
CO_FOAM	4	5	4	4	3
PES_0.1	4	5	4	4	4
PES_0.5	4	5	4	4	4
PES_FOAM	4	5	4	4	4

At first, these tests were performed on all three cotton samples to assess which one presented the most desirable behavior in a product. Cotton was chosen not only because it has a more pleasant hand feel than polyester, but also because Tintex has a preference for working with cotton, as it is a natural fiber. Table 9 shows the results of these tests. The water repellency was evaluated on a scale of 0-5 according to AATCC test method 22, where 0 means complete wetting of the entire face of the specimen and 5 means no sticking or wetting of the specimen face. Of the cotton samples, it was chosen the CO_0.5 sample since it presented the highest water resistance and repellency, and the lowest air permeability.

These tests were then performed in the polyester sample (PES_0.5) to evaluate how a different fiber influences these functional characteristics. When compared with the cotton sample it presents a higher water resistance (0.32 m H₂O compared to 0.14 m H₂O) and repellency (rating 5 compared to 3), which can be attributed to the hydrophobic nature of polyester fibers. It also shows a higher air permeability (0.10 cm³·cm⁻²·s⁻¹ compared to 0.05 cm³·cm⁻²·s⁻¹), probably due to the lower grammage of this knit. Grammage is directly proportional to fabric thickness, which means that if the knit has a lower thickness, it makes it easier for air to permeate.

Table 9 - Results of the resistance to water, water repellency, and air permeability tests

Sample	Resistance to water (m H ₂ O)	Water repellency	Air permeability (cm ³ ·cm ⁻² ·s ⁻¹)
CO_0.1	0.00	1	1.13
CO_0.5	0.14	3	0.05
CO_FOAM	0.07	2	0.08
PES_0.5	0.32	5	0.10

4.3 Chemical, mechanical and morphological characterization

The samples that proceeded to the characterization phase were the CO_0.5 because within the cotton samples it was the one that showed the most promising results, and PES_0.5 to evaluate the influence that a different substrate can have chemically and physically at a more fundamental level.

4.3.1 Scanning Electron Microscopy

The coating surface on both cotton and polyester knits was investigated through SEM analysis (Figure 16). The coating surface is very similar on both cotton and polyester knits and shows clear irregularities, such as the craters that appear on the entire coating surface. These craters may be caused by foam bubbles (formed during the mixing of the formulation compounds) which have broken at the air interface of the coating^[44] or by the formation of water vapor bubbles inside the coating that eventually reach the surface, creating craters. In the cross-sectional SEM images of the CO_0.5 sample, particularly in Figure 17(B), it is possible to observe that the coating fills in the interstitial spaces of the knit, demonstrating a good wettability of the surface. Figure 17(A) shows that the coating thickness is irregular, ranging from 62 μm to 103 μm , which can be attributed to the irregular structure of the knit. Comparing with the thickness measured with the outside micrometer (90 μm), it is possible to conclude that this value is not representative of the entire surface.

To understand if the craters that appear in the coating surface only arise in this specific formulation or if it is normal to appear in other coatings applied as a paste, SEM analysis was performed in a coating applied as a paste (0.2 mm of thickness) previously developed by Tintex. It is observed in the cross-sectional image (Figure 18(B)) that the coating wraps around each fiber, rather than forming a “flat” layer over the knit, as seen in the CO_0.5 sample. This sample also shows significantly fewer craters (Figure 18(A)). However, it also has a lower coating thickness, leading to the conclusion that the appearance of craters is related to the coating thickness.

The morphological properties of the cotton and polyester uncoated knits, as well as the raw knits, were also investigated using microscopic images (Appendix C).

4.3.2 Fourier Transform Infrared - Attenuated Total Reflectance

FTIR-ATR analysis was performed to identify the chemical composition of the coating and to analyze whether it would be chemically homogeneous regardless of the substrate. The overlapping of the spectra of the CO_0.5, PES_0.5, and the coating by itself samples is shown in Figure 19.

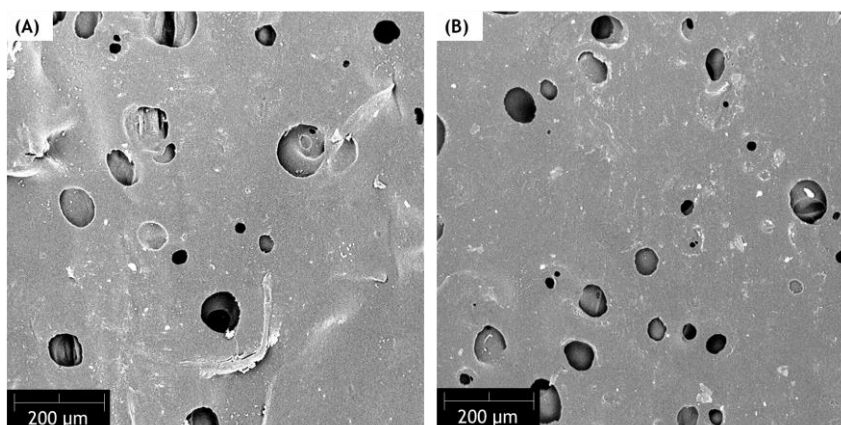


Figure 16 - SEM images of the coating surface on (A) PES_0.5, and (B) CO_0.5 samples with a magnification of 300x.

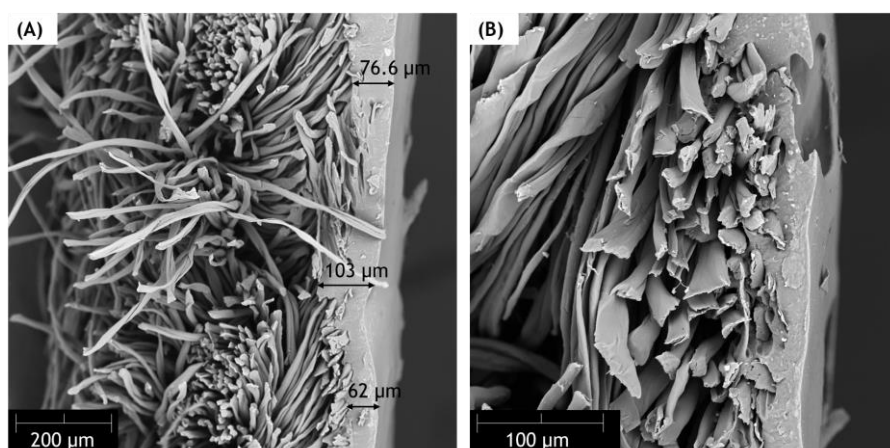


Figure 17 - Cross-sectional images of the CO_0.5 sample at different magnifications: (A) 300x and (B) 800x.

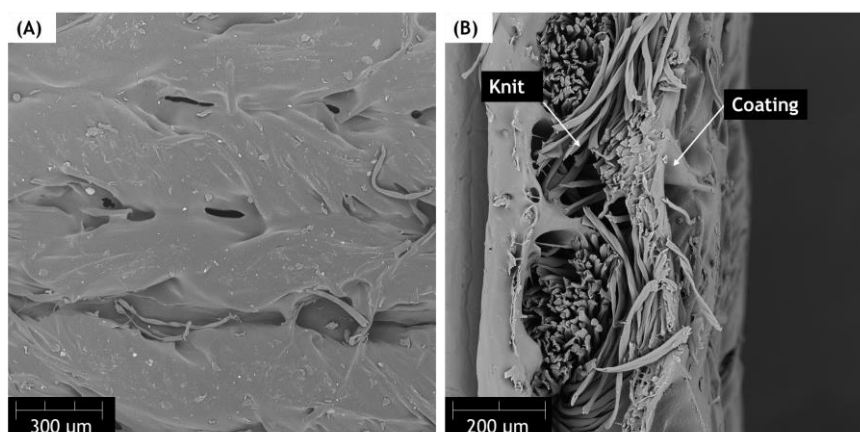


Figure 18 - Tintex paste coating (0.2 mm application thickness) SEM (A) surface and (B) cross-sectional images with a magnification of 200x.

Since the two spectra of the two knits with different natures are almost completely coincident between each other and the coating, it is possible to conclude that the infrared

(IR) radiation can only reach the coating layer, and therefore, these spectra correspond to the coating spectrum. In fact, the IR radiation has a penetration depth of 2 μm , and the final coating thickness is higher in both cases (90 μm in the cotton sample, and 130 μm in the polyester sample). Considering the composition of the formulation with three binders, two of a polyurethane type and one of an acrylic polymer, it was possible to recognize the bands corresponding to these materials.

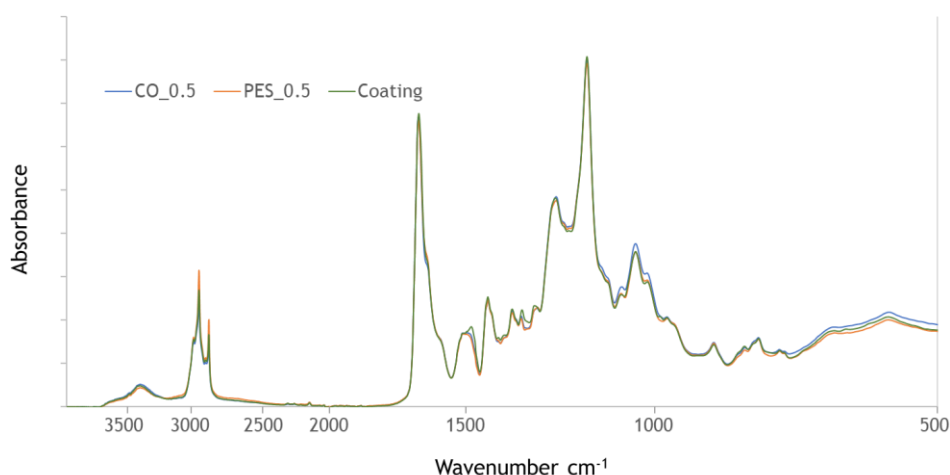


Figure 19 - Normalized FTIR-ATR spectra of the CO_0.5, PES_0.5, and coating by itself samples.

A broad absorption band of the N-H stretching from the urethane group is seen at 3356 cm^{-1} . The sharp peaks at 2917 and 2850 cm^{-1} correspond to CH_2 asymmetric and symmetric stretching, respectively, from the aliphatic part of the coating. The intense peak at 1726 cm^{-1} is related to the C=O stretching from carbonyl groups. At 1540 cm^{-1} is seen a peak corresponding to the N-H bending. The peak related to the CH_2 bending vibration found in aliphatic compounds is seen at 1463 cm^{-1} . The stretching band of C-O from the urethane and acrylate binders appears in 1000-1150 cm^{-1} .

The raw and treated cotton and polyester knits spectra were also obtained so as to achieve a better comprehension of the substrates and their finishing (Appendix D).

FTIR analysis was also performed in the samples with a thickness of application of 0.1 mm. Since the final coating thickness is smaller than that of the CO_0.5 and PES_0.5 samples, it is expected that the IR radiation will be able to reach closer to the substrate/coating interface. The second derivatives of the spectra of both samples with 0.1 mm and 0.5 mm of thickness, the respective substrates, and the coating were obtained in order to better visualize the differences in band intensities (Figures 20 and 21). It is possible to observe that the second derivative spectra of the CO_0.5 and PES_0.5 samples are very close to the coating spectrum, while the second derivative spectra of the CO_0.1 and PES_0.1 samples are further away to the coating spectrum and closer to the spectra of the respective substrates.

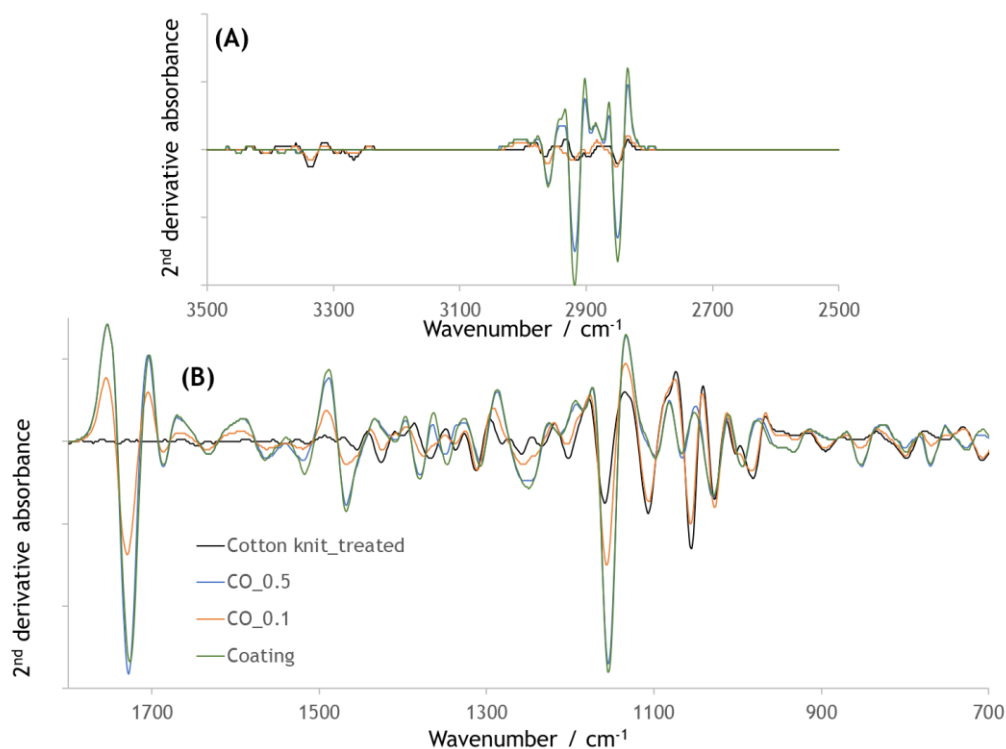


Figure 20 - Normalized second derivatives of the spectra of the CO_0.1, CO_0.5, treated cotton knit, and coating by itself samples in the regions between (A) 2500 cm^{-1} and 3500 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1} .

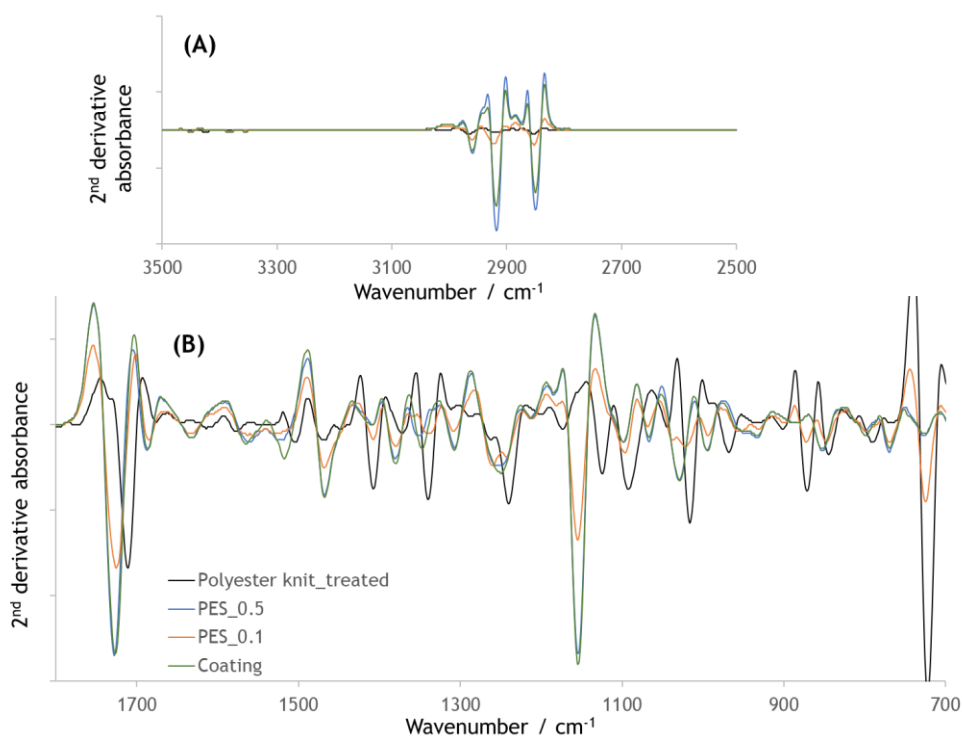


Figure 21 - Normalized second derivatives of the spectra of the PES_0.1, PES_0.5, treated polyester knit, and coating by itself samples, in the regions between (A) 2500 cm^{-1} and 3000 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1} .

In the overlay of the CO_0.1, CO_0.5, treated cotton knit, and coating FTIR-ATR spectra (Figure E-1) is possible to observe that the peaks that appear around 2900 cm^{-1} in the CO_0.1 spectrum are very similar to the peaks related to CH_2 stretching of the cotton knit spectrum. Furthermore, from the peak that appears around 1150 cm^{-1} until 500 cm^{-1} , this zone of the CO_0.1 spectrum is almost equal to the equivalent zone of the cotton knit spectrum. This can be explained by the low intensity peaks that this zone of the coating spectrum shows, resulting in a higher contribution of the substrate bands. In the overlay of the PES_0.1, PES_0.5, treated polyester knit, and coating FTIR-ATR spectra (Figure E-2) is detected a new peak at 723 cm^{-1} in the PES_0.1 spectrum, which can be attributed to the very strong peak related to the out-of-plane $=\text{C-H}$ bending of the benzene ring observed in the treated polyester knit spectrum. The analysis of these spectra leads to the conclusion that the lower the coating thickness, the lower the contribution of the coating to the composite, and consequently, the less the benefits that it can provide. This is the reason why a greater permeability to air and water is observed in the CO_0.1 and PES_0.1 samples.

An intensity peak ratio analysis of the second derivatives of the spectra of CO_0.1, CO_0.5, PES_0.1, and PES_0.5 samples was performed (Table 10), between the peaks referring to the coating bands and the reference CH_2 stretching peak, as it is a very stable band, in order to get a quantitative sense of the difference observed in these peaks. It was also analyzed the intensity peak ratio between the out-of-plane $=\text{C-H}$ bending of the benzene ring band of the polyester samples and the reference peak. The intensity peak ratios between CH_2 stretching and C=O stretching, and CH_2 stretching and C-O stretching, are inferior to 1 in both substrates, which indicates that the C=O and C-O bands are the most intense in the coating spectrum. It is also possible to infer that the ratios of CO_0.1 and PES_0.1 are inferior when compared with CO_0.5 and PES_0.5, due to a higher overshadowing of the CH_2 band peak of the coating by the substrate bands. Regarding the polyester samples, as expected, the ratio between CH_2 stretching and the out-of-plane $=\text{C-H}$ bending of the benzene ring is substantially inferior in the PES_0.1 than in the PES_0.5, because the intensity of this peak is much higher in the PES_0.1 spectrum than in the PES_0.5.

Table 10 - Intensity peak ratios (normalized second derivative absorbance) of the CO_0.5, CO_0.1, PES_0.5, and PES_0.1 spectra

Band	$I_{\text{CH}_2}/I_{\text{band}}$			
	CO_0.5	CO_0.1	PES_0.5	PES_0.1
C=O stretching (1726 cm^{-1})	0.23	0.09	0.39	0.12
CH_2 bending (1463 cm^{-1})	0.84	0.45	1.27	0.40
C-O stretching (1155 cm^{-1})	0.24	0.08	0.39	0.15
$=\text{C-H}$ bending (723 cm^{-1})	-	-	8.4	0.22

4.3.3 Raman spectroscopy

Confocal Raman imaging combines Raman spectroscopy with a confocal microscope. The Raman microscope acquires the information of a complete Raman spectrum at every image pixel, resulting in an image with two different colors, where one color is attributed to the knit spectrum and the other color is attributed to the coating spectrum. Raman depth-profiling images are shown in Figure 22 and they show that in some zones the coating fills in the interstitial spaces of the knit, corroborating the conclusions drawn by the SEM analysis. Moreover, in Figure 22(A) the interruption of the coating by one of the craters is noticeable. Additional obtained Raman images are shown in Figures F-1 and F-2.

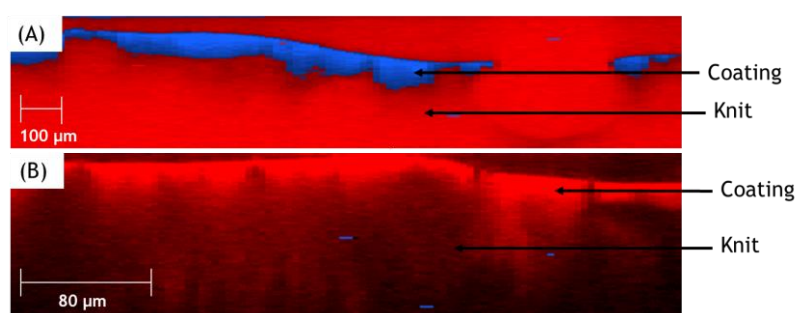


Figure 22 - Raman depth-profiling images of the samples (A) CO_{0.5} and (B) PES_{0.5}.

In order to try to understand if there were different chemical bonds between the coating and the different substrates, the two samples were analyzed with Raman spectroscopy, since this equipment scans 100 points per line and each one of these points is a spectrum, thus making it possible to acquire a spectrum from a point closer to the coating/substrate interface. The Raman spectra of the coating in the CO_{0.5} and PES_{0.5} samples are represented in Figure 23. The Raman spectra of the coating are very identical in the two samples, as expected.

Raman and IR spectroscopy are complementary techniques for the structural analysis of any molecule. The Raman effect results from an inelastic Raman scattering of light by vibrating molecules, whereas IR spectroscopy relies on the absorption of light by vibrating molecules. Molecules with functional groups that have strong dipoles display strong peaks in the IR, whereas functional groups that have weak dipoles and readily undergo a change in polarizability display strong peaks in Raman.^[45] The strong peaks at 2941 cm⁻¹ and 2939 cm⁻¹ in the CO_{0.5} and PES_{0.5} samples, respectively, correspond to the CH₂ stretching band. The CO_{0.5} sample peak at 1753 cm⁻¹ and the PES_{0.5} sample peak at 1745 cm⁻¹ are related to the C=O stretching band. At 1481 cm⁻¹ there is a peak in the CO_{0.5} sample, that also appears at 1464 cm⁻¹ in the PES_{0.5} sample, that corresponds to the CH₂ bending band. Nonetheless, the existence of any chemical bond that has not been observed in the IR spectrum is not verified.

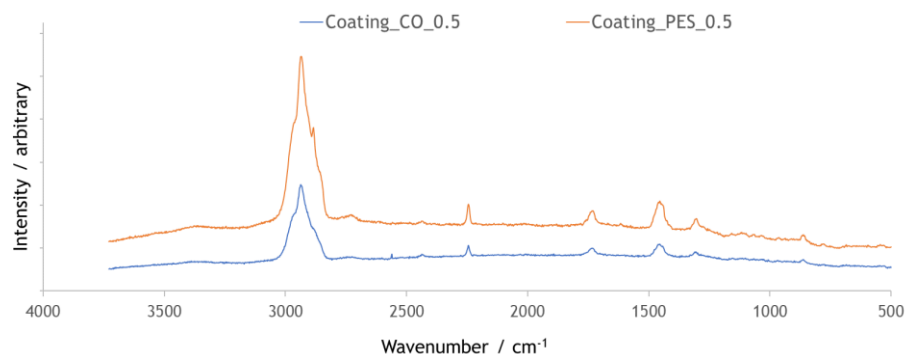


Figure 23 - Raman spectra of the coating in the CO_0.5 and PES_0.5 samples.

4.3.4 Thermal analysis

DSC and TGA curves of the coating by itself are represented in Figures 24 and 25, respectively. Besides some instrumental noise, the DSC curve does not show any reaction and thermal transition, meaning the sample is fully cured. If there were unreacted functional groups in the coating, they could continue to react under the elevated temperatures of the DSC, resulting in an exothermic peak.^[17] From the thermal analysis software, it is possible to obtain the onset temperature (point in the TGA curve where a deflection is first observed from the established baseline prior to the thermal event^[46]), which is approximately 325 °C, meaning the thermal degradation begins at this temperature. The TGA curve also shows a 92% decrease in the mass sample. The differential thermogravimetric (DTG) curve has two peaks (inflection points), at approximately 347 °C and 392 °C, which correspond to the temperature where the weight loss rate is maximum. The two inflection points indicate that the decomposition takes place in two successive steps.

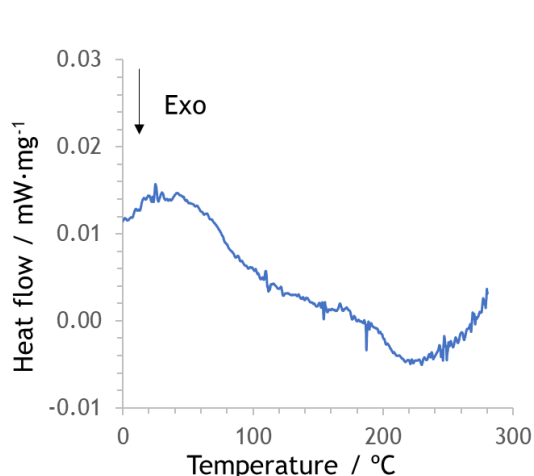


Figure 24 - DSC curve of a sample of the coating by itself.

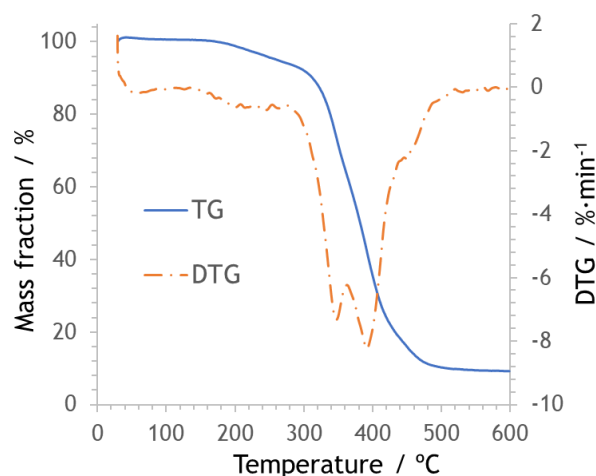


Figure 25 - Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of a sample of the coating by itself.

Figures 26 and 27 show the DSC and TGA curves of the PES_0.5 sample. In the DSC curve, it is possible to see a melting point at approximately 249 °C. The melting point of poly(ethylene terephthalate) (PET) fabric mentioned in the literature is 255 °C^[47], so it can be deduced that this melting peak corresponds to the melting of the PET knit. The reason for the small difference between these temperatures may be in the different conditions of DSC analysis and in the fact that PET with different molecular weights will have different melting temperatures. From the TGA graph is possible to infer that this sample has a two-step degradation process: the first step from the weight loss process started at about 306 °C, reaching its peak at 335 °C; the second step happened from 394 °C, with an inflection point at 432 °C. The latter step may be assigned to the decomposition of PET chains^[48], leading to the conclusion that the first step is related to the decomposition of the coating. The total weight loss of the sample was 88%.

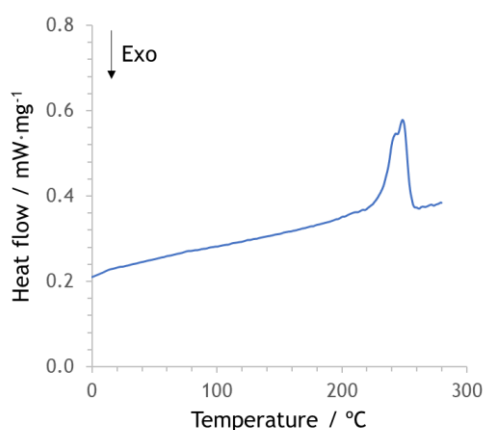


Figure 26 - DSC curve of the PES_0.5 sample.

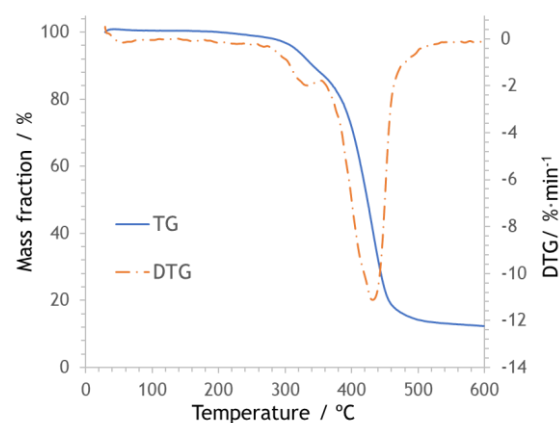


Figure 27 - TG and DTG curves of the PES_0.5 sample.

Through the DSC curve of the CO_0.5 sample (Figure 28), it is possible to infer that no reaction and thermal transition occurs. The only thermal event that is usually expected in a cotton fabric is an endotherm between 330 °C and 385 °C related to the decomposition of cellulose^[49], but it is not shown in this graph since the sample was heated only up to 280 °C. The TGA curve (Figure 29) shows an initial weight loss of about 3%, which is related to the loss of moisture that typically occurs below 100 °C in cotton fabrics. The onset temperature of degradation is approximately 354 °C, exhibiting its maximum weight loss rate at 379 °C, corresponding to the decomposition of cellulose.^[50] The total weight loss of the sample was 89%. Unlike the TGA curve of the polyester sample, this does not show a two-step degradation process, since the thermal degradation of cotton initiates first than that of polyester, and in this case, the coating degradation is not seen. Through the TGA and DSC curves of this sample, it is possible to infer that the coating does not interfere with the thermal stability of the cotton knit.

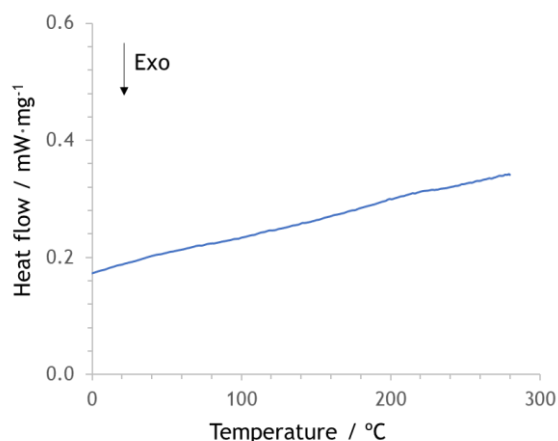


Figure 28 - DSC curve of the CO_{0.5} sample.

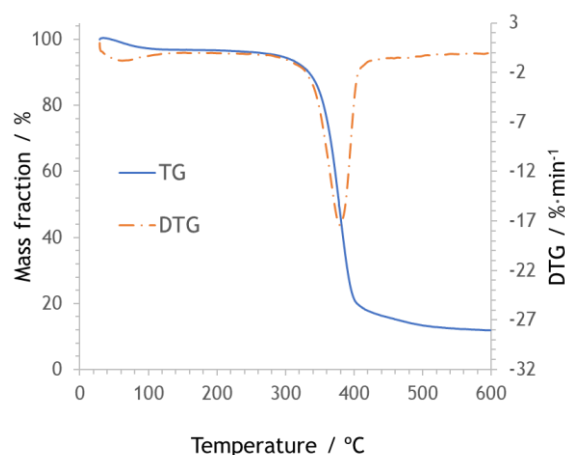


Figure 29 - TG and DTG curves of the CO_{0.5} sample.

4.3.5 Breaking strength

The breaking strength is one of the most important performance properties of a knitted fabric since it contributes to the durability of the fabric. A coated knit is expected to have a higher breaking strength, both longitudinally and transversely, since the crosslinking agent may increase the stiffness of the knit.^[51,52] In fact, in Figure 30 it can be observed that the breaking strength of the coated samples is higher than that of the uncoated samples, both longitudinally and transversely. The CV of the measurements is below 30% (except for the transverse breaking strength of the CO_{0.5} sample), so it is possible to conclude that the coating has a reinforcement effect on the knit. However, it was not possible to obtain the results of the longitudinal breaking strength of the uncoated cotton knit, since in these tests the knit stretched without tearing.

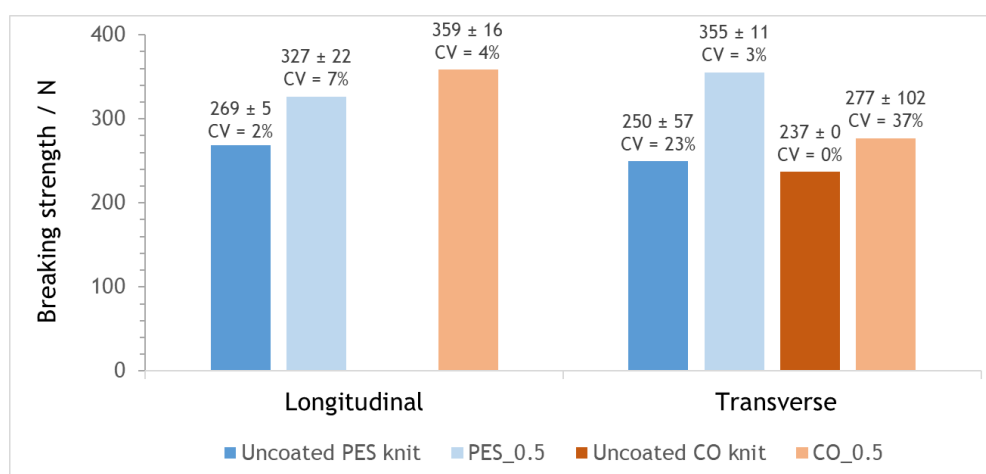


Figure 30 - Longitudinal (direction of the lengthwise loops) and transverse (direction of the crosswise loops) breaking strengths of the uncoated treated polyester and cotton knits, and the PES_{0.5} and CO_{0.5} samples.

4.4 Validation of bluesign® product requirements

As mentioned previously, cotton was the substrate chosen to develop this product. Therefore, in order to proceed with the bluesign® certification of this product, an internal validation of the requirements of bluesign® regarding the CO_0.5 sample was carried out. First, it was defined the usage range A, since most of the clothing items, which is the principal focus of this product, fall into this range. The next step was to validate the consumer safety limits requirements:

- The determined pH of the aqueous extract of the textile was 6.6, thus it is within the acceptable range.
- The product does not emit any unpleasant odor.
- Since this product is not intended for babies, the color fastness to saliva and perspiration parameter does not need to be validated.
- All chemical substances used in the coating were selected through Bluesign Finder.
- All Tintex cotton knits references are a bluesign® product, hence all consumer safety limits and bans related to the dyes and chemical substances used in the knit are within acceptable limits for bluesign®.

Since all parameters mentioned above meet the criteria required by bluesign® to receive the bluesign® product label, it is then possible to apply the CO_0.5 sample for certification by bluesign®.

4.5 Coating formulation improvement

After the validation of bluesign® product requirements, it was attempted an improvement of the coating formulation applied on the cotton knit (composition described in Table 3). In order to try not only to reduce the number of craters observed through the presence of craters in the SEM images, but also to increase the resistance to water and water repellency, and its overall quality, the coating formulation was improved by:

- Increasing the viscosity of the blend to 75 dPa·s, not only because a higher viscosity allows a reduction in the appearance of foam bubbles, but also because it allows an easier application of the coating on the knit, thus reducing the probability of occurring application related problems.
- Adding an anti-foaming agent - Antimussol SFE liquid - to try to decrease the number of foam bubbles formed during the mixing phase, and consequently decrease the number of craters that appear on the surface.

- Reducing the mass fraction of water to help increase the viscosity and to prevent the appearance of foam bubbles caused by the intensive stirring of water.
- Reducing the mass fraction of Tubicoat SHM (foam stabilizer), so that the foam bubbles that eventually form do not maintain their dynamic stability and disappear over time.
- Adding a compound that provides a hydrophobic effect - Nuva N2155 liq - to increase the resistance to water penetration.

It is also important to note that both added compounds (Antimussol SFE liquid and Nuva N2155 liq) are also bluesign® approved.

The water resistance and water repellency tests were carried out in a sample of the new paste formulation applied on the cotton knit with 0.5 mm of application thickness. It was obtained a hydrostatic head of 0.20 m H₂O regarding the water resistance, presenting a higher water resistance when compared with the CO_0.5 sample (0.14 m H₂O). The water repellency test received the rating 3, the same as the CO_0.5 sample.

SEM analysis was also performed on this sample to verify if the existence of craters on the coating surface persisted (Figure 31). It is once more possible to observe the existence of craters, leading to the conclusion that this is a persistent feature of paste applications. Moreover, the thickness is higher than that of the CO_0.5 sample, ranging from 130 µm to 173 µm, which can be attributed to the appearance of larger craters inside the coating.

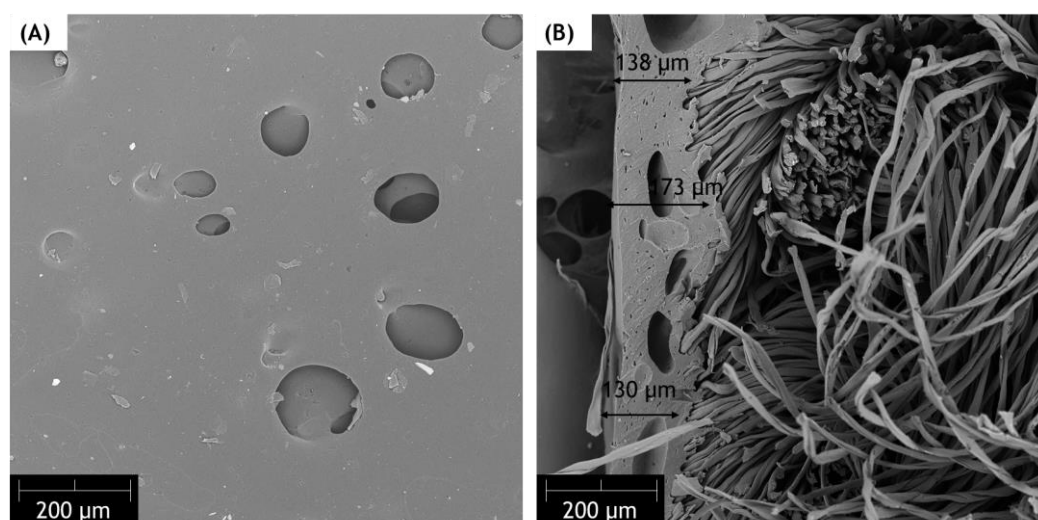


Figure 31 - Sample of the improved formulation applied on the cotton knit SEM (A) surface and (B) cross-sectional images.

5 Conclusion

This dissertation envisioned the development of a fully bluesign® approved coating formulation and the study of its impact on the final product. The coating was applied as a paste with two different application thicknesses, 0.1 mm and 0.5 mm, and as a stable foam with an application thickness of 0.5 mm, in two different substrates: cotton and polyester interlock knits.

Several textile quality control tests were performed in order to select the sample that presented the better performance outcome: Martindale abrasion and pilling tests, dry and wet rubbing color fastness test, Pilling Box test, wash resistance test, air permeability test, water resistance test, and water repellency test. Based on the results obtained, the paste with an application thickness of 0.5 mm was selected, standing out for its good wash resistance, low air permeability, and greater water resistance and repellency than the other samples. Regarding the substrate, it was selected the cotton knit because it presented a smoother hand feel and because the company prefers working with cotton.

For a better comprehension of the influence of the different knits, a chemical, mechanical and morphological characterization was performed on the samples of the paste with 0.5 mm of application thickness applied on both knits. A SEM analysis allowed the observation of craters on the surface and inside the coating, which could be due to foam bubbles that have broken at the air interface or an irregular drying in depth. It was also concluded that the emergence of these craters is correlated with the relatively large thickness of the coating. The spectra obtained by FTIR-ATR and Raman spectroscopies confirmed the predominance of the polyurethane and acrylic polymer binders in the coating composition, and that it is chemically consistent regardless of the substrate. DSC and TGA analysis proved that the samples were fully cured. The determination of the breaking strength of the coated and uncoated knit allowed to conclude that the breaking strength is higher in the coated than in the uncoated samples.

In order to proceed with the development of a product based on this coating applied on the cotton knit, the requirements demanded by bluesign® were validated. The final step of the dissertation was the improvement of the coating formulation, by changing the mass fraction of the foam stabilizers and water and adding an anti-foaming agent and a hydrophobic agent. This improvement led to a better water resistance of the sample.

6 Assessment of the work done

6.1 Objectives Achieved

This dissertation main objective was the study and development of a coating formulation composed only of bluesign® approved chemical substances, in order to obtain a product capable of receiving the bluesign® label. In this respect, several tests of textile quality control and characterization were performed, also allowing the study of the impact of the substrate, coating thickness, and state of application in the product performance. The bluesign® coating formulation was successfully developed and the mentioned testes allowed a better comprehension of the formulation and the final product.

6.2 Limitations and Future Work

The biggest limitation found during the dissertation was the limited access to FEUP equipment due to the restrictions of the COVID-19 pandemic, delaying the execution of the characterization tests.

In addition to the main objective of the dissertation, another ongoing work is the industrialization of this product, where greater control of properties such as the viscosity during all the mixing phase and air bubble purge can be achieved.

In the future, other important features, such as water vapor permeability, which determines the product breathability, could also be tested. It would also be interesting to study the reason for the emergence of craters at the surface and inside the coating. If it is due to irregular drying, a SEM analysis of the sample after drying could be performed, studying various drying temperatures. Since the craters are related to the thickness, and the calendering/embossing processes influence the final coating thickness, various processing conditions of these equipment could be tested. It would also be relevant to perform a more in-depth study on the interfacial phenomena between the substrate and the coating, and their influence on the entire coating process.

6.3 Final Assessment

In general, the development of this dissertation was very interesting on a personal level, in the way that it allowed to acquire knowledge about textiles and the textile industry and to deepen my knowledge about polymeric materials and their characterization techniques. In addition, this dissertation addresses a very ongoing theme - sustainability - which led me to look deeply into the area of sustainable innovation in the textile sector, an area in which Tintex is an industry leader.

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Appendix A Processes implemented by Tintex Textiles, S.A.

There are several processes implemented by Tintex to treat the textiles before they reach the coating process. The treatment that the substrate receives is very important because it contributes to the overall performance of the coating by influencing the substrate/coating interactions.

1. Scouring

Textile materials have impurities immediately after manufacturing that need to be removed for better dyeing or printing. These impurities come in natural form in the case of natural fibers (waxes, proteins, pectic substances, and mineral matters), but also as added oils, sizes, and other foreign matter in yarn and fabric manufacturing. Scouring consists of a cleaning process with soap or detergent, with or without the addition of alkali, that removes these impurities. This process, in addition to purifying, also imparts the hydrophilic character necessary for the subsequent processes.^[53]

2. Thermo-setting/bleaching

In the next step, the type of treatment is different for synthetic fibers (e.g. polyester) and natural fibers (e.g. cotton).

The synthetic fibers may form creases and wrinkles at high temperatures and retain these deformations at lower processing temperatures due to their thermoplastic nature. In addition, thermal shrinkage or thermal expansion may be observed, creating difficulties in garment manufacturing. To eliminate these thermal distortions, the polyester fibers require an operation called thermo-setting. This operation is carried out in a stenter machine while the material is heated to a certain temperature in order to supply enough energy to the fiber to change the crystallinity and orientation of the fibers, whilst the material is held to optimized conditions.^[53,54]

The natural fibers such as cotton, even after scouring, contain residual coloring matter providing a yellowish or brownish appearance to these fibers. For this reason, the cotton fibers need to undergo a special treatment called bleaching. The object of bleaching is to remove natural and adventitious coloring matters with the help of bleaching agents with minimum degradation of the fiber to produce white fabrics.^[53,55]

3. Anti-pilling treatment

Pilling is a process that occurs in fabrics formed from spun yarns, especially cotton knitted fabrics, in which loose fibers separate from the yarn due to rubbing, external pressure, or fiber-fiber friction, and then intertwine with each other and appear on the surface of the fabric, resulting in the formation of pilling. This is an undesirable process

because it affects the appearance and shortens the product life cycle. For this reason, the fabrics must be submitted to an anti-pilling treatment, whether chemical or enzymatic.^[56]

The chemical anti-pilling treatment consists of using special chemicals that suppress the ability of fibers to slacken and reduce the mechanical resistance of the fiber.^[57]

Enzymes such as cellulases, hemicellulases, and pectinases are used in enzymatic anti-pilling treatment, as they are proteins capable of catalyzing specific chemical reactions of organic materials. This provokes the pills to fall off from the fabrics, reducing the pilling tendency.^[57]

4. Mercerization

This step is optional, and it is employed according to the desired end-use. Mercerization consists of a treatment of cotton yarns with a caustic soda solution in order to swell the cotton fiber, resulting in increased luster, tensile strength, dimensional stability, and dyeability.^[53]

5. Dyeing

Dyeing is a process in which is produced a uniform coloration throughout the substrate to match a pre-selected color. The most common methods for the application of color are exhaust dyeing (batch), continuous (padding), and printing.^[53]

The method utilized in Tintex is exhaust dyeing, performed in a pressurized jet dyeing machine. It is classified as exhaust dyeing because the textile is dyed contacting with a bath of dyes and auxiliaries, during a certain amount of time and a certain temperature profile (Figure A-1). The dyeing profile is composed of an adsorption phase and a diffusion phase. The process starts at ambient temperature and the temperature is gradually increased until a certain temperature according to the type of dye.^[53]

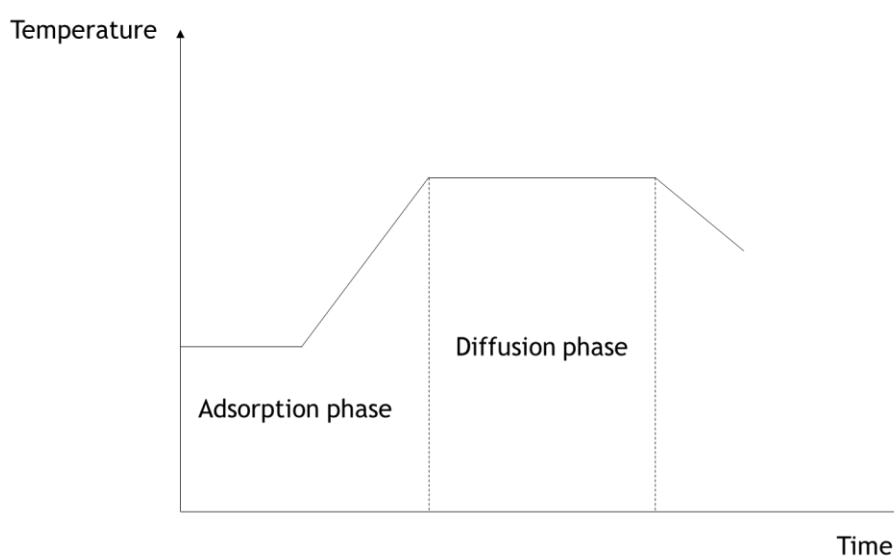


Figure A-1 - Exhaust dyeing temperature profile. Adapted from [53].

First is introduced the textile into the jet machine and then the auxiliaries are added into the dyebath and allowed to circulate in order to enable uniform concentration throughout the dyebath and substrate surface. The dyes are then introduced and again allowed to circulate before the temperature is increased. The process culminates in equilibrium when the dye concentration in the fiber and the dyebath does not change significantly. It is considered that the dye was completely absorbed by the substrate surface and that there is only a small concentration of dye left in the dyebath. The resulting shade should be uniform and must match the pre-selected color. Otherwise, small additions of dye may be made to achieve the required shade.^[53]

The type of dye used varies accordingly to the nature of the fiber that is going to be dyed. Disperse dyes are predominantly used in polyester fibers, while reactive dyes are used in cotton fibers.^[53]

6. Drying and squeezing

After the dyeing process, the textile is thoroughly washed, squeezed in a tubular squeezing machine and then sent for drying.

7. Thermo-setting

After these processes, the polyester fibers need to be stabilized and thermo-set again in order to center the fibers.

8. Finishing

Before the substrate is coated it needs to receive a finishing treatment in order to improve the coating outcome. At Tintex, the most common treatment that the textile is given is a bath with an anionic thermo-reactive polyurethane to impart hydrophilicity, thus giving guarantees that the coating will spread evenly over the substrate. In addition, this thermo-reactive polyurethane used is also a softener. Softeners raise flexibility and result in a soft, smooth, and flexible handle.^[58]

Appendix B Equipment used during the course of the dissertation

All the equipment utilized during the samples preparation is represented in Figures B-1 to B-7.



Figure B-1 - METTLER TOLEDO precision balance.



Figure B-2- IKA EUROSTAR 20 digital mechanical stirrer.



Figure B-3 - Thermo Scientific HAAKE Viscotester 2 Plus.



Figure B-4 - Werner Mathis Lab Coater&Dryer type LTE-S.



Figure B-5 - Teng FG20100 feeler gauge set with 20 blades (0.05 - 1.0 mm).



Figure B-6 - Monti Antonio roll calender model 93-2000sp.



Figure B-7 - MIB-Messzeuge outside micrometer.

Some of the equipment utilized for the quality control tests is illustrated below in Figures B-8 to B-11.



Figure B-8 - James Heal Pilling Box.



Figure B-9 - Crockmeter.



Figure B-10 - James Heal Spray Rating Tester.



Figure B-11 - TEXTTEST Air Permeability Tester FX 3300 LabAir IV.

Some of the equipment utilized in the chemical, mechanical and morphological characterization is shown below in Figures B-12 to B-14.



Figure B-12 - Thermo Fischer Scientific Phenom XL scanning electron microscope.



Figure B-13 - NETZSCH STA 449 F3 Jupiter.

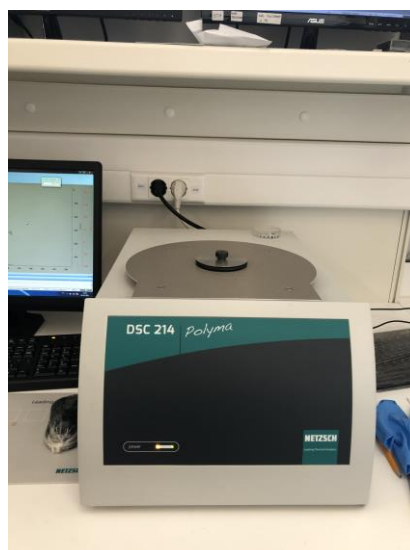


Figure B-14 - NETZSCH DSC 214 Polyma calorimeter.

Appendix C SEM analysis of the knits

Figure C-1(A,C) shows the polyester and cotton raw knits, respectively, and Figure C-1(B,D) shows the treated polyester and cotton knits. When comparing cotton with polyester fibers, it is possible to conclude that polyester fibers tend to be more compact, which is expected due to their synthetic nature. In Figure C-1(B,D) is observed more particles (indicated by red arrows), which can be attributed to the polymeric finish that the knits receive before they are coated. The same figure shows a better orientation of the fibers when compared to the raw knits, especially in the cotton, since the polymeric finish can impart dimensional stability.

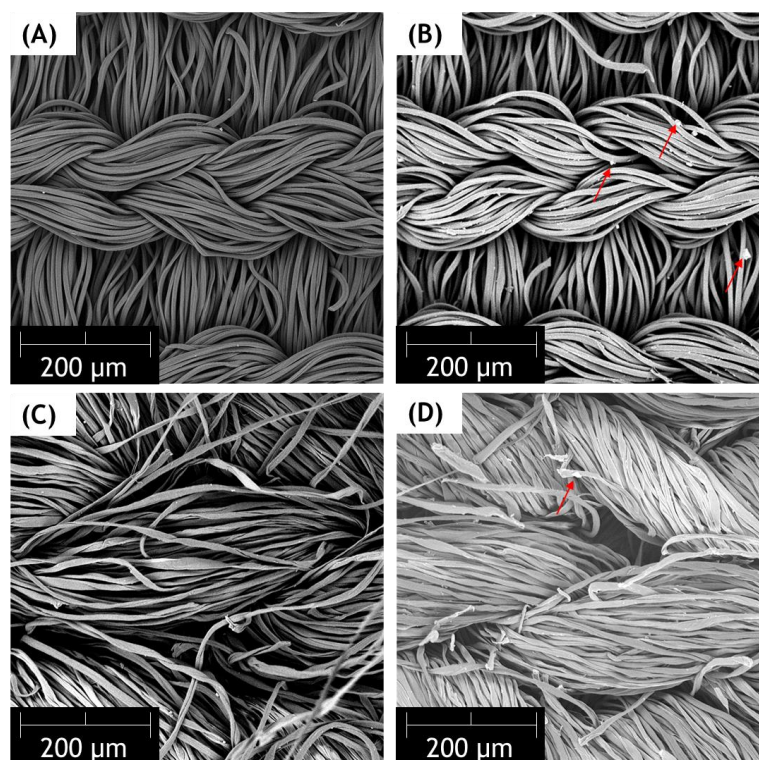


Figure C-1 - SEM images of (A) raw polyester knit, (B) treated polyester knit, (C) raw cotton knit, and (D) treated cotton knit.

Appendix D FTIR-ATR spectra of the knits

Before the cotton knit was coated, it was treated with the thermo-reactive polyurethane dispersion (Hydroperm RPU New Liq C).

The spectra of the cotton knit treated with the polyurethane finishing and of the raw cotton knit (not treated) are illustrated in Figure D-1. Since it is mainly constituted by cellulose (Figure D-2), it is mostly identifiable cellulose related peaks in both spectra, such as -OH stretching between $3335\text{--}3290\text{ cm}^{-1}$, CH_2 asymmetric and symmetric stretching at 2899 cm^{-1} and 2850 cm^{-1} respectively, and C-O stretching between $1204\text{--}1000\text{ cm}^{-1}$.^[59] In addition, there is a peak related to H_2O adsorbed molecules, typical of cotton fabrics, between $1650\text{--}1615\text{ cm}^{-1}$, which is at lower intensity in the treated cotton knit due to some water being evaporated from the knit during drying of the polymeric finish. Furthermore, at 799 cm^{-1} appears a peak in the treated cotton knit that could be related to some of the compounds used in the formulation of Hydroperm RPU New Liq C. The second derivatives of the spectra above mentioned are shown in Figures D-3.

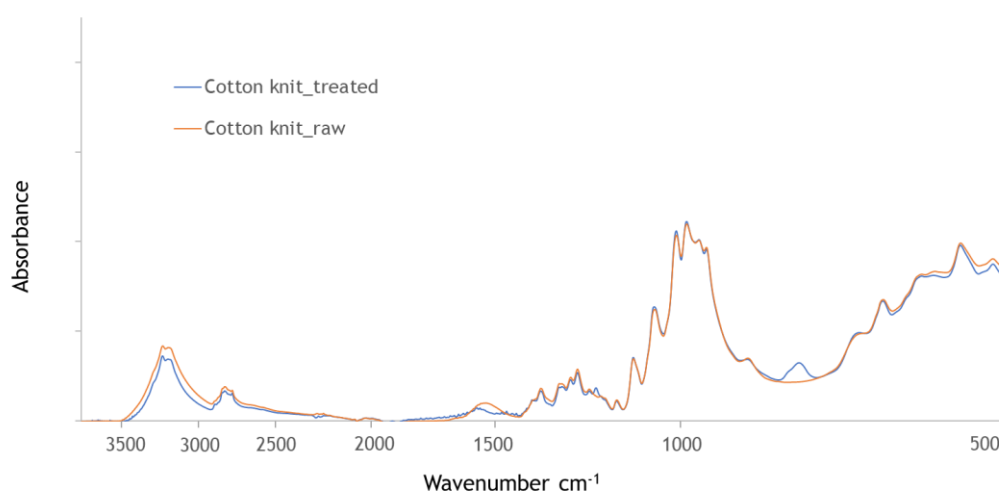


Figure D-1 - Normalized FTIR-ATR spectra of the raw cotton knit and the treated cotton knit.

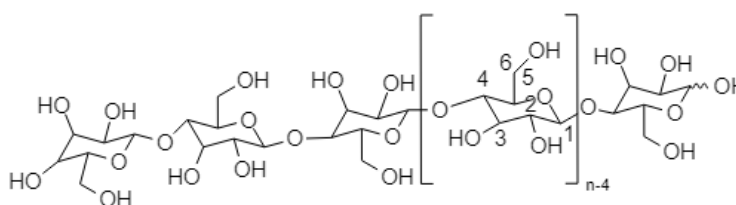


Figure D-2 - Molecular structure of cellulose (n = degree of polymerization). Adapted from [60].

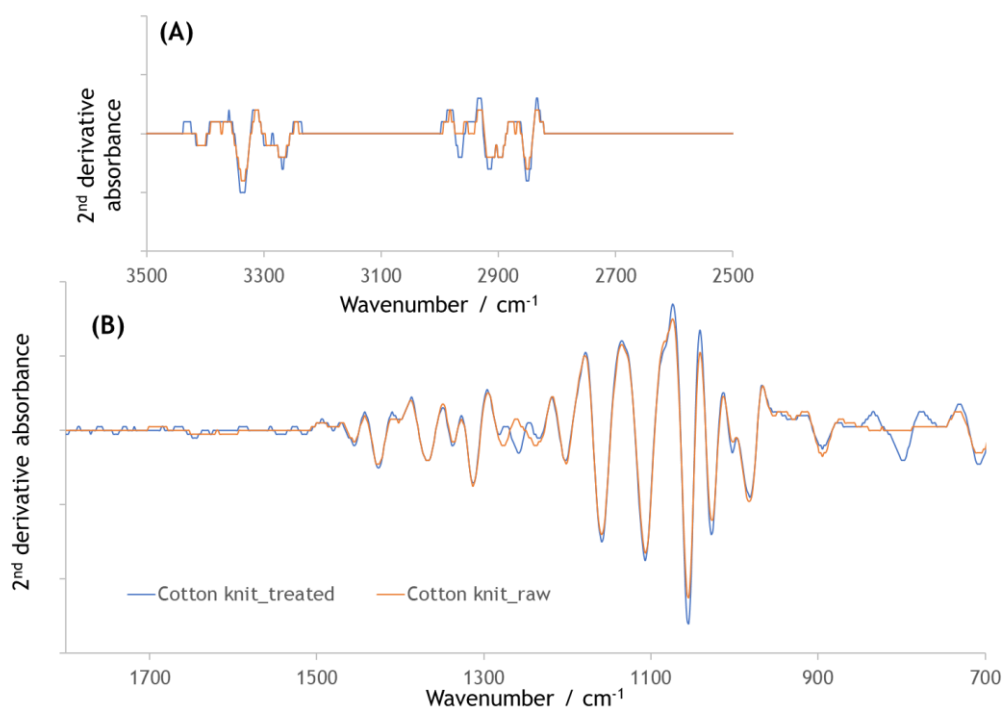


Figure D-3 - Normalized second derivatives of the spectra of the treated and raw cotton knits in the region between (A) 2500 cm^{-1} and 3500 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1} .

An intensity peak ratio analysis was performed to have a quantitative perception of the influence of the finishing in the intensity of the peaks (Table D-1). The CH_2 symmetric stretching band was used as a reference for this comparison, due to being a very stable band. As it can be seen, the ratio of the peaks (intensity of the peak referring to the CH_2 symmetric stretching band divided by the intensity of the peaks referring to the other cellulose related bands) is very similar between the treated and the raw.

Table D-1- Intensity peak ratios (normalized second derivative absorbance) of the treated and raw cotton knits spectra

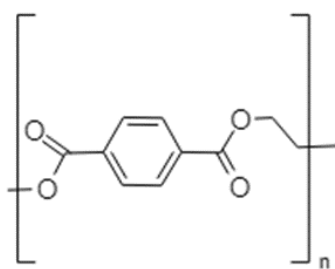
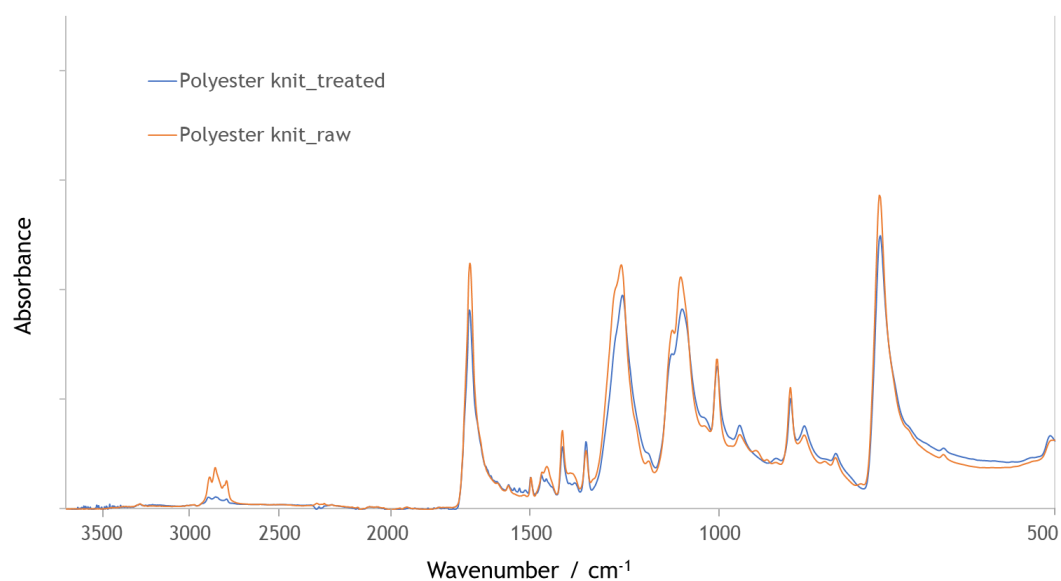
Band	$I_{\text{CH}_2}/I_{\text{band}}$	
	Treated cotton knit	Raw cotton knit
OH stretching (3336 cm^{-1})	0.80	0.75
C-O stretching (1054 cm^{-1})	0.08	0.07

The polyester knit received a different finishing than the cotton knit, whose composition is described in table D-2.

Table D-2 - Polyester knit finishing composition

Commercial name	Chemical basis	Function
Nuva N2155 liq.	Dispersion of a fluorine compound	Hydrophobic agent
miDori WA 1.0	Aqueous emulsion of a microalgae oil	Hydrophilic softener
Arkophob DAN New liq	Polyurethane dispersion	Crosslinker
Kielaron MRZ liq	Polyglycol ether derivative	Surfactant

The polyester knit is made of PET fiber, whose structure is represented in Figure D-4. The peaks of the IR spectra are congruous with this structure (Figure D-5), like C-H stretching around $2965\text{--}2853\text{ cm}^{-1}$, C=O and C-O stretching at 1712 cm^{-1} and 1240 cm^{-1} , respectively, from the ester group, =C-H bending of the benzene ring at 871 cm^{-1} , and out-of-plane =C-H bending of the benzene ring at 723 cm^{-1} . The second derivatives of the treated and raw polyester knits spectra are shown in Figure D-6.

**Figure D-4 - Poly(ethylene terephthalate) (PET) structure. Adapted from [61].****Figure D-5 - Normalized FTIR-ATR spectra of the raw polyester knit and the treated polyester knit.**

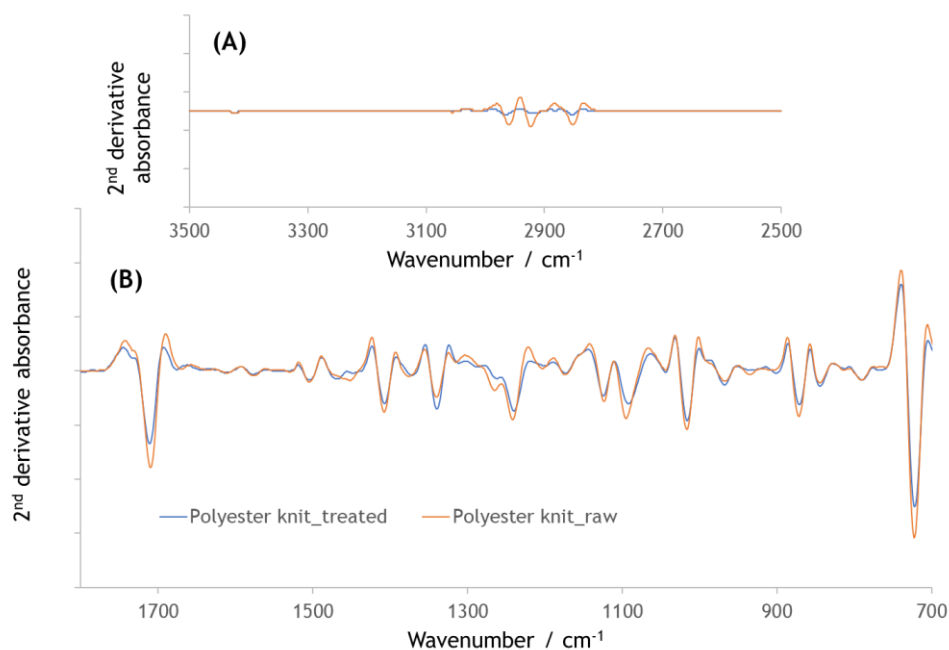


Figure D-6 - Normalized second derivatives of the spectra of the treated and raw polyester knits in the region between (A) 2500 cm^{-1} and 3500 cm^{-1} , and (B) 700 cm^{-1} and 1800 cm^{-1} .

Figure D-6 shows that the raw polyester knit peaks are more intense than the treated polyester knit peaks, meaning the finishing may be “masking” the polyester bands. The only peak where the treated knit is more intense is the one at 1340 cm^{-1} that could be related to the C-N stretching band from an imide group formed during the curing process of the polyurethane dispersion (Arkophob) used in the finishing.^[62] The intensity peak ratio analysis was once again performed using the C-H stretching band as a reference. As it can be seen from Table D-3, the ratio between C-H stretching and C=O stretching is lower in the treated than in the raw knit, which can be explained by the higher contribution with C=O bonds from the microalgae oil (miDori WA 1.0) of the finishing since it is mainly constituted by fatty acids. The higher the number of C=O bonds, the higher the intensity of this peak, resulting in a lower intensity of the C-H peak, since a C=O bond has a higher dipole moment than a C-H bond. Moreover, the ratio between C-H stretching and C-N stretching is lower in the treated knit, due to the presence of Arkophob as explained before. The other ratios are very similar between each other.

Table D-3 - Intensity peak ratios (normalized second derivative absorbance) of the treated and raw polyester knits spectra

Band	I_{C-H}/I_{band}	
	Treated polyester knit	Raw polyester knit
C=O stretching (1712 cm^{-1})	0.03	0.08
C-N stretching (1340 cm^{-1})	0.06	0.29
C-O stretching (1240 cm^{-1})	0.05	0.16
C=C bending (871 cm^{-1})	0.06	0.17
=C-H bending (723 cm^{-1})	0.02	0.05

Appendix E FTIR-ATR spectra of the CO_0.1 and PES_0.1 samples

The FTIR-ATR spectra of the CO_0.5, CO_0.1, treated cotton knit, and coating by itself samples are represented in Figure E-1.

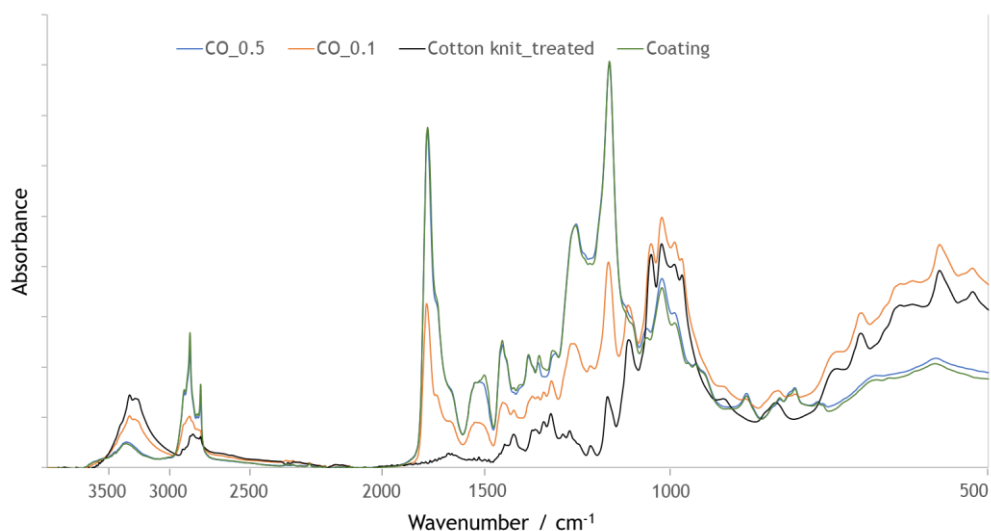


Figure E-1 - Normalized FTIR-ATR spectra of the CO_0.1, CO_0.5, treated cotton knit, and coating by itself samples.

Figure E-2 shows the FTIR-ATR spectra of the PES_0.1, PES_0.5, treated polyester knit, and coating by itself samples.

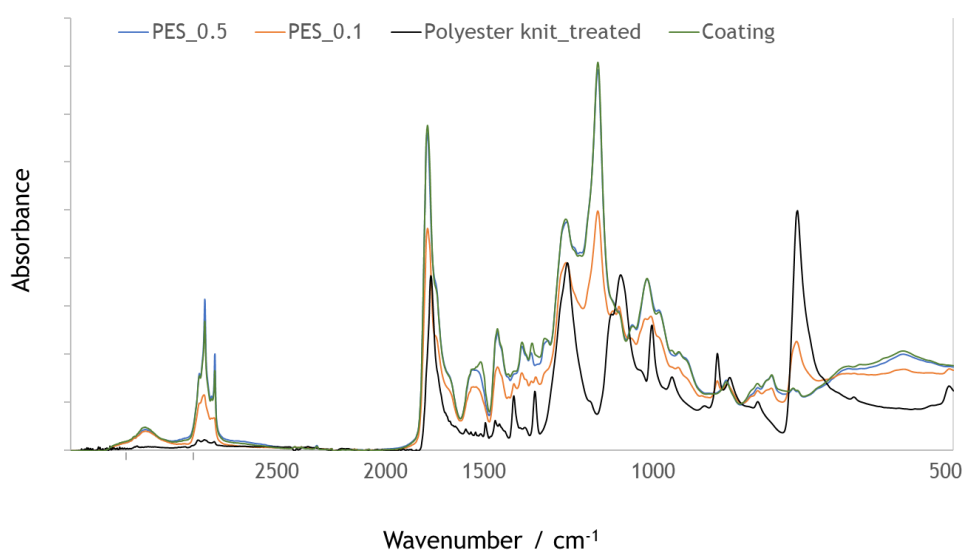


Figure E-2 - Normalized FTIR-ATR spectra of the PES_0.1, PES_0.5, treated polyester knit, and coating by itself samples.

Appendix F Confocal Raman imaging

Figures F-1 and F-2 show the correlative Raman-SEM and confocal color-coded Raman images of the CO_0.5 and PES_0.5 samples, respectively.

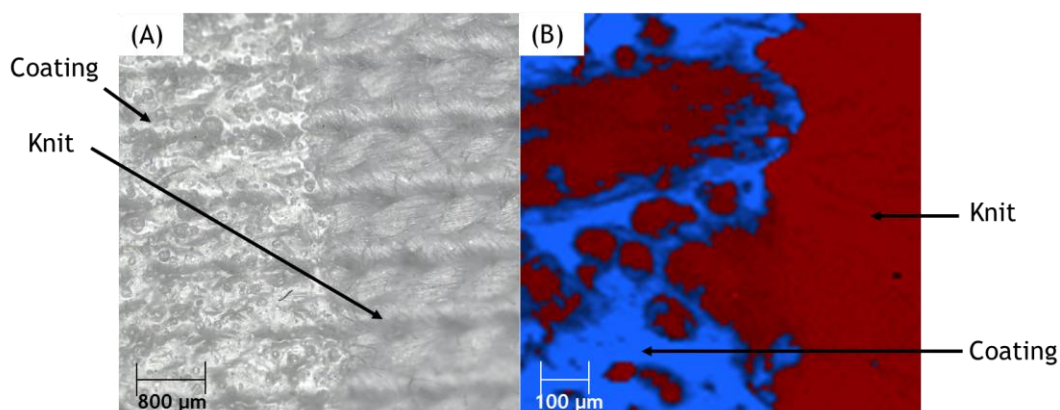


Figure F-1 - Raman imaging of the CO_0.5 sample: (A) Correlative Raman-SEM image; (B) Confocal color-coded Raman image of the area marked in (A).

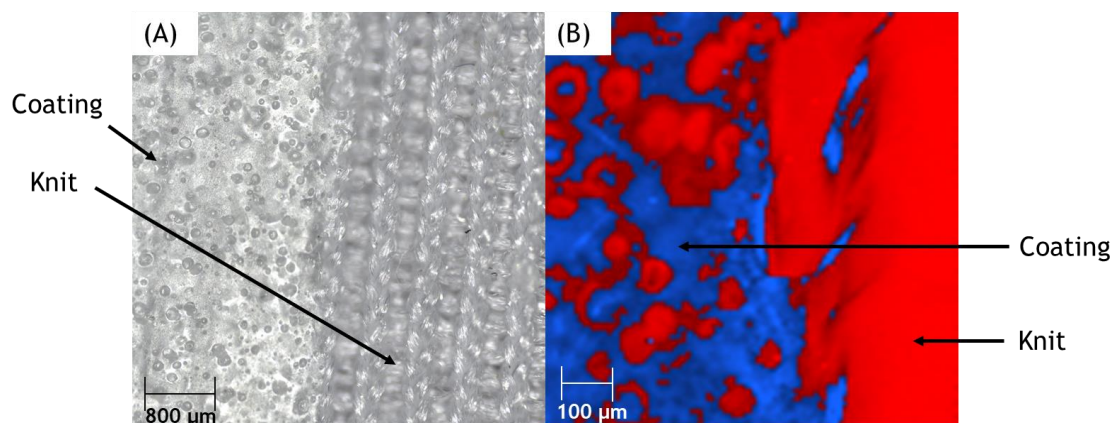


Figure F-2 - Raman imaging of the PES_0.5 sample: (A) Correlative Raman-SEM image; (B) Confocal color-coded Raman image of the area marked in (A).