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SURFACE MODIFICATION OF COTTON YARNS AND MIXED FIBRE KNITWEAR FOR IMPROVED PERFORMANCE

Summary of the Doctoral Thesis



RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Design Technologies

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for review to Riga Technical University for promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for promotion to a scientific degree.

Ieva Baķe (signature)

Date:

The Doctoral Thesis has been written in Latvian. It consists of an Introduction, 4 chapters, conclusions, 75 figures, and 16 tables; the total number of pages is 125. The Bibliography contains 131 titles.

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ABBREVIATIONS

HT– hydrothermal
ATR-FTIR – attenuated total reflection Fourier transform infrared spectroscopy
FT – functional textiles
ST – smart textiles
TEOS – tetraethyl orthosilicate
ZAD – zinc acetate dihydrate
CO – cotton
PA – polyamide
PES – polyester
UV – ultraviolet radiation
TR– thermal resistance
AP – air permeability
VP – vapour permeability
SEM – scanning electron microscopy
Zn – zinc
wt.% – percentage of mass volume
FFE – full factorial experiment
EDX – energy dispersive X-ray spectroscopy

1. GENERAL DESCRIPTION OF THE THESIS

Introduction

Textiles made by knitting technologies are an ideal framework for creating flexible functional system elements in clothing and maintaining wearing comfort [1]. Knitted underwear, hosiery and sportswear are comfortable to use as the first layer of clothing in contact with the wearer's body [2]. At the same time, it is also a structure that provides favourable living conditions for diverse microorganisms and accumulates both them and pollution caused by the body and the environment, resulting in the need for regular hydrothermal treatment of the products. On the other hand, the components of electronic systems, especially those made of electrically conductive threads, even with very gentle hydrothermal treatment regimens, rapidly lose their functional properties in contact with detergents [3–6].

Although the technological possibilities of knitting allow creating flexible electronic system elements (sensors, wires, generator components, displays, etc.) in the process of manufacturing the textile itself, which is a big step forward in the development of wearable electronics [4],[5],[7], there remain unsolved problems of how to ensure the normal operating process of the relevant textile. Solutions are being sought [8]:

- 1) the option in which the components of the electronic system must be removable before the hydrothermal treatment, therefore they cannot be produced in the process of textile knitting;
- 2) creating a new generation of flexible electronic system components that do not lose their functional properties during wear and hydrothermal treatment processes;
- 3) modifying the textile itself by adding additional properties in the process along with its characteristic properties, which ensure the need for milder hydrothermal treatment less often, reducing the temperature, consumption of detergents and their aggressiveness.

Topicality of the Doctoral Thesis

Textiles, especially knitted ones, offer ideal conditions for microorganism habitats, such as large specific surfaces with good adhesion and water retention properties and optimal temperatures provided by the wearer. Therefore, there is a great need for finishes that facilitate care and increase the time between hydrothermal treatment cycles, as well as antimicrobial finishes that protect textile fibres from degradation under the influence of microorganisms and bio growths on textiles in the outdoor environment, which would make a less favourable habitat for bacteria, thus reducing odour formation that occurs in the metabolic processes of bacteria living in sweat, as well as protect users from the transmission and spread of pathogens; in addition, in the case of smart clothing, the functional properties of the components of the electronic system would be preserved longer.

By choosing to modify textiles by adding additional properties in the process along with its inherent properties, it is possible to subject them together with the embedded wearable electronics components to a gentler hydrothermal treatment, as well as to increase the time between treatments, reducing the consumption of energy and detergents and their aggressiveness. At the same time, in the process of creating smart textiles, the task of compromise must be solved, harmonizing the functional characteristics important to the wearer with those necessary for the safe operation of the elements of the electronic system and ensuring stable operating parameters both in the integrated manufacturing and operation process. In this context, the problems solved in the course of modification of knitted fabric or yarn before the knitting process during which functional electronic system elements are incorporated, are relevant because wearable electronics have many advantages – they can collect large amounts of useful data about the user, but together with the supporting textile are exposed to wear processes that rapidly reduces the performance of electronic system elements.

The Aim of the Thesis

Multifunctional modification of the surface of cotton yarn, cotton/polyamide (CO/PA), and cotton/polyester (CO/PES) knitwear and evaluation of the effect of modification on the functional properties and wearing comfort characteristics of knitted products.

Tasks of the Thesis

- Create an analytical review of the modification of yarn, cotton, and mixed fibre textiles.
- Modify industrially knitted cotton/polyamide sock products of mixed fibre composition, evaluate the changes in functional properties caused by the modification and their impact on wearing comfort.
- Apply sol-gel technology to multifunctional modification of cotton yarn and evaluate the effect of modification on the physical and mechanical properties of the yarn.
- Develop a technological sequence of yarn preparation and knitting to produce a knitted fabric of plated plain weave of mixed fibre composition – modified cotton yarn/PA/PES.
- Perform a comparative analysis of the modified knitted fabric variants and evaluate the effects of the yarn modification on functional and wearing comfort characteristics.
- Formulate summaries, recommendations, and conclusions.
- Present the acquired know-how in publications and scientific conferences.

Scientific Novelty

As a result of the study of the possibilities of functionalization of cotton/PA and cotton/PES industrially knitted platinized plain knit sock products of mixed fibre composition, the adapted technology for the modification of platinized knitted sock products with a silicon-based sol with zinc acetate dihydrate included in it as a precursor allows to increase the wear resistance of knitted products of this class, to ensure easy care (water and dirt repellence) effect and antibacterial effect in the textile interface area with the wearer's skin. As a result of the study, the effectiveness of the functionalization of sock products with a mixed fibre composition and the possibility of including the adapted modification technology in the industrial technological sequence by integrating it into the final hydrothermal treatment unit has been proved.

Technologies have been developed for modifying the cotton yarn, preparing it for knitting and obtaining a platinized plain knit of mixed fibre composition with a modified cotton yarn (Patent LV15500B). The inclusion of the modified yarn in platinized plain weave knitting in one modification process provides several additional functions for improving the performance of the sock product, not exposing the wearable electronic components integrated in the knitting process to the relatively aggressive modification technological parameters and maintaining their performance during the modification process of the knitted sock product.

The ATR FTIR spectra processing and interpretation methodology adapted within the work grants the opportunity to obtain comparative qualitative and quantitative evaluations of the influence and modification effects of the technological process parameters of textile threads and mixed fibre composition platinized plain weave knitwear without destroying the test samples, and the necessary corrections are quickly developed.

Practical Significance of the Thesis

Platinized plain cotton and yarn cotton/synthetic sock products include a range of assortment groups with a very wide range of applications in casual, sports, leisure, and work wear sets, as well as in products with integrated wearable electronics. They are usually worn for a long time, subjecting the textiles and the electronics embedded in them to combined cyclical deformations in an adverse environment. Traditionally, sock products need to be washed frequently to ensure wearing comfort, thus gradually reducing their performance and consuming resources.

The functionalization methods developed in the Thesis make it possible to modify industrially made sock products of mixed fibre composition and to create new technologies by

integrating ~ 75–80 % modified cotton yarn in the knitting process, in both cases providing additional functions such as improved wear resistance, antimicrobial activity and surface self-cleaning effect, thus extending the wear time between washes while maintaining the required level of wearing comfort and reducing the consumption of detergents, electricity and water, and the associated combined effect of environmental pollution, thus increasing the product's lifespan.

The adapted ATR-FTIR spectra processing and interpretation methodology is an easy-to-use control tool for evaluating the influence of technological and modifying compositions and parameters of their application processes and for their adjustment based on the obtained data, as well as for the analysis of coating stability. It could be equally useful in the field of the development of new textile and modification methods and processes and as a control tool in the production, use, and recycling/disposal processes.

Theses to be Defended

1. Modification of mixed fibre composition cotton/polyamide industrially knitted platinized plain weave sock products with silicon-based sol, modified with zinc acetate dihydrate precursor integrated into it ensures antibacterial effect of socks and easy cleaning effect and increases wear resistance, as well as maintains properties that ensure wearing comfort.
2. Applying the additionally processed data obtained in the process of Fourier transform infrared spectroscopy, it is possible to obtain not only qualitative, but also quantitative data for evaluating the influence and modification effects of technological process parameters of platinized plain knit knitted fabric of mixed fibre composition.
3. By applying the developed technology to the modification of cotton yarn in the sol-gel process, the mathematical description created as a result of the study of the physical and mechanical properties of the process parameters in the form of regression equations and two-dimensional contour plot of the response surface allows to predict the physical, mechanical, functional, and comfort-providing properties of the modified yarn and knitted structure depending on the modification process parameters. The mathematical description of the study of the physical and mechanical properties of the parameters of the cotton yarn sol gel modification process technology created during the Doctoral Thesis in the form of regression equations and two-dimensional contour plot of the response surface allows to predict the physical, mechanical, functional, and comfort-providing properties of the modified yarn and knitted structure, depending on the modification process parameters.
4. Up to 30 % functionalization of knitted fabric of mixed fibre composition with polyamide and polyester fibres can be ensured by incorporating the cotton yarn components modified in the platinized structure in the knitting process, without exposing the wearable electronics components integrated in the knitting process to the aggressive functionalization process parameters, thus maintaining the long-term performance of the wearable electronics.

Approbation of the Results

Articles in scientific journals indexed in Web of Science and Scopus database

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Publications of the author of the research not related to the topic of the Thesis

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Patent

- **Ieva Baķe**, Dana Beļakova Silvija Kukle, Zane Zelča, “Method for Assigning Additional Functional Properties by Modifying Textile Yarn for Knitted Products”, *Patent No. LV15500B*, 2021.

2. OVERVIEW OF THE THESIS

2.1. Situation Analysis

The textile industry is one of the largest and most important manufacturing sectors worldwide, where trends are rapidly developing by combining traditional knowledge with industrial and technological advances creating products with high added value [9].

Functional textiles (FT) cover a wide spectrum of textiles classified according to different principles divided into six large groups based on functions (Table 2.1). Textile products with health-related functions like antibacterial, deodorizing, being impervious to mould and protection from infrared radiation may eliminate or hinder the growth and reproduction of bacteria and other microorganisms, repel or eliminate microbes and viruses, protect and improve human health and prevent disease.

Table.2.1

Classification of FTs According to their Properties [10]–[14]

Class	Provided function
Comfort function	<ul style="list-style-type: none"> • Single-wizard effect • Protection against weather • Thermoregulation and antistatic properties
Protection	<ul style="list-style-type: none"> • Protection against ultraviolet (UV) radiation, chemicals, electromagnetism, punctures, splinters, noises • Thermal protection • Medical fasteners
Medicine	<ul style="list-style-type: none"> • Protection against bacteria, mosquitoes, odours, mites, infrared radiation
Smart textiles	<ul style="list-style-type: none"> • Biological and physiological monitoring, telemedicine • Wireless monitoring, remote data management • Shape memory • Reaction to external stimuli (colour change, etc.)
Easy to clean	<ul style="list-style-type: none"> • “Easy to clean” properties • Protection against creasing • Antibacterial and antimicrobial properties • Resistance to strong cleaning agents • Anti-fingerprints • UV protection • Air purification

There are different types of functional finishes that can be applied depending on the type of the textile fibre and the desired end use.

Surface modification can be divided into two categories: wet/chemical and physical modification process. The first category includes material surface nano treatment processes in which a colloidal solution or its dispersion is used to improve and provide various additional functions to textile materials [15].

This type of functional finish has various advantages:

- smaller number of nanomaterials and bulk materials used in finishing compared to the traditional types of finishing;
- the finish does not affect the aesthetic appearance and feel of the textile;
- coatings are more durable, as the surface area and volume ratio of nanomaterials is increased and a uniform coating of the textile material is ensured;
- possibility to assign additional functions [16].

2.2. Technologies of Experiments and Sample Testing Methods

Industrially knitted cotton 81 % / PA19 % socks and 100 % cotton yarn (linear density 24 tex) were subjected to the functionalization in the sol gel process.

Sol Synthesis and Modification Technology

The synthesis and modification technology of sol is based on the method developed by Dr. Svetlana Vihodceva in her Doctoral Thesis [17]. The reagents used for the synthesis of the sol solution are summarized in Table 2.2.

Table 2.2

List of Used Reagents			
REAGENTS	FORMULA	MANUFACTURER	CONCENTRATION, %
TETRAETHYL ORTHOSILICATE (TEOS)	$C_8H_{20}O_4Si$	ACRÖS, OORGANICS Belgium	$\geq 98 \%$
ETHANOL	C_2H_5OH	EU (distributor “Enola” Ltd)	$\geq 99.98 \%$
HYDROFLUORIC ACID	HF	SIGMA-ALDRICH Germany	$\geq 40 \%$
ZINC ACETATE DIHYDRATE (ZAD)	$Zn(CH_3COO)_2$ H_2O	CHEMPUR Poland	analytically pure
ACETIC ACID	CH_3COOH	CHEMPUR Poland	$\geq 99.98 \%$

Silicon alkoxide (TEOS) has been used in the synthesis of the sol. Ethanol was added to TEOS. Then, while stirring the solution, distilled water with HF or acetic acid was added, which was further heated to a temperature of 50 °C for 30 minutes. Then, zinc acetate dihydrate (ZAD) was added; the solution was heated while stirring for 10 minutes until a homogeneous dispersion was obtained and the zinc compound was dissolved [17]. During the modifications, the ratio of solution to the weight of the samples was optimized for some groups of samples to reduce the amount of excess solution and to observe the effect the changing ratio on the comfort and mechanical properties. Uniform pressing of the samples was applied with a calender. The samples were hang-dried until dry. After that, heating of the samples was applied, varying the temperature and heating time (all variants are summarized in Table 2.2).

2.3. Sample Preparation for Modification and Post-processing

Hydrothermal Treatment

All samples before and after treatment were subjected to hydrothermal (HT) treatment in accordance with the standard ISO 6330:2021 [18], which specifies a gentle washing regime at 30 °C temperature for 46 minutes using 5 g/l standard detergent without phosphate and optical brighteners – *SDC Enterprise Limited. 2304 Standard Soap*. The cotton yarn was boiled at 100 °C and then washed by hand ensuring maximum uniformity and similar conditions and rinsed 2 times in distilled water. After washing, the samples were dried at room temperature.

Additional Processing of Samples Before Modification

Additional pre-treatment steps were applied to some sample groups. The samples were treated in a solution of water and acetone (ratio 1 l water and 500 ml acetone) for 10 minutes and rinsed 2 times in distilled water. Cotton yarn was washed at 100 °C and rinsed in distilled water before modification.

Processing of Modified Yarn Samples into Knitted Fabrics

Loose looped yarn bundles – hanks – were prepared from the cones before hydrothermal (HT) treatment and/or modification, as it makes easier for the yarns to accept sol solution and dry as the strands are loose. The modified yarns on cones suitable for use with knitting machine were prepared on cross cone winder (professional wool winder *Brother KA-719*). The modified cotton yarns together with PA or PES threads combined with elastane were processed into a plated plain weave knit on a single-cylinder sock knitting machine (*Lonati*, 14-th gauge, 156 needles, 3 ½ inches).

Evaluation of Parameters Characterizing the Structure of Knitted Textiles

All knitted samples have the following characteristic sizes:

- composition, %: the exact fabric composition is determined by dividing a 200 mm² sample area into thread units – cotton, polyamide (polyester) and elastane threads, the exact weight of which is obtained using analytical scales *Techniport. Typ PRLT T5*, EN 12127:1997 [19];
- Knitwear density in the horizontal (b_h) and vertical (b_v) directions as the arithmetic mean of three parallel measurements of the number of stitches in an area of 100 mm² in the horizontal and vertical directions, EN 14971:2006 [20].

2.4. Characteristics and Transcripts of the Tested Samples

In general, the processed and tested samples can be divided into three groups:

- industrially produced cotton 81 % / PA 19 % socks and 100 % PA woven fabric;
- cotton yarn (linear density 24 tex);
- experimental knits from modified cotton yarn and unmodified PA, or PES threads combined with elastane.

Factorial design experiment Plans 2² and 2³ were used to prepare the samples with the following mathematical modelling using regression equations and geometric interpretations in the form of 2D contour plots [21] and the correlation and distribution analysis of the samples characteristics used for data analysis and reliability assessment.

Table 2.3

Sample Designations and Their Transcripts

Designation	Modif.	Catalyst		Sample pre-treatment		ZAD mas. %		Mass of the samples against the volume of the solution in the sol, g/ml			Consolidation temperature, °C		Consolidation time, min				HT processing after modif.	Right/left side of the jersey FTIR tests	
		HF	CH ₃ OOH	Washed	Acetone	5	7.5	8	10	12	100	120	5	8	10	15		Right	Left
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ks1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		-
Ks2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ms1			-		-					-	-			-	-				-
Ms2			-		-					-	-			-	-			-	-
H7.5/120/8			-		-					-	-			-	-			-	-
HE7.5/120/8					-					-	-			-	-			-	-
7.5/-100/8M			-		-					-	-			-	-			-	-
7.5/-120/8M			-		-					-	-			-	-			-	-
7.5/-100/8A			-	-						-	-			-	-			-	-
7.5/-120/8A			-	-						-	-			-	-			-	-
A5-100/5			-	-						-	-			-	-			-	-
A5-100/8			-	-						-	-			-	-			-	-
A5-120/5			-	-						-	-			-	-			-	-
A5-120/8			-	-						-	-			-	-			-	-
M5-100/5			-		-					-	-			-	-			-	-
M5-100/8			-		-					-	-			-	-			-	-
M5-120/5			-		-					-	-			-	-			-	-
M5-120/8			-		-					-	-			-	-			-	-
MM5-100/5			-		-					-	-			-	-			-	-
MM5-100/8			-		-					-	-			-	-			-	-

Table 2.3 continued

Designation	Modif	Catalysator		Sample pre-treatment		ZAD mas.%		Mass of the samples against the volume of the solution in the sol, g/ml			Consolidation temperature, °C		Consolidation time, min				HT processing after modif.	Right/left side of the jersey FTIR tests	
		HF	CH ₃ OOH	Washed	Acetone	5	7.5	8	10	12	100	120	5	8	10	15		Right	Left
MM5-120/5			-		-		-											-	-
MM5-120/8			-		-		-											-	-
M7.5-100/5			-		-		-											-	-
M7.5-100/8			-		-		-											-	-
M7.5-120/5			-		-		-											-	-
M7.5-120/8			-		-		-											-	-
MM7.5-100/5			-		-		-											-	-
MM7.5-100/8			-		-		-											-	-
MM7.5-120/5			-		-		-											-	-
MM7.5-120/8			-		-		-											-	-
M/1:10/10			-		-		-											-	-
M/W/1:10/10			-		-		-											-	-
MWT/1			-		-		-											-	-
MWT/2			-		-		-											-	-
MWT/3			-		-		-											-	-
MWW/4			-		-		-											-	-
M/W/1:8/5			-		-		-											-	-
M/W/1:8/15			-		-		-											-	-
M/W/1:12/5			-		-		-											-	-
M/W1:12/15			-		-		-											-	-

2.5. Testing Methods of Mechanical and Comfort Properties

Before modification and testing, the samples were kept in climate chamber *Binker KBF 115* for 24 hours under normal climate conditions (temperature 20 ± 2 °C, relative humidity 65 ± 5 %) according to the standard [22].

Determination of Yarn Strength

The breaking strength of the yarn when stretched is one of the main indicators of quality. The strength of the yarn is determined by pulling machines, where internal stresses occur in the material under the influence of load; when the maximum limit is reached, the material breaks. Number of samples – 100 in each set of tested samples. Sample clamping length – 500 mm, suitable pretension 12 cN ($0.5 \text{ cN/tex} \pm 0.1 \text{ cN/tex}$), clamp movement speed 500 mm / 1 min according to standard [23], resulting from yarn density – 24 tex.

Equipment used:

- Tensile strength tester *PM-3-1*. Clamping length 200 mm, number of samples 100. Tested threads were weighed on analytical scales *Techiport. Typ PRLT T5* with an accuracy of 0.0001 g.
- Universal testing equipment *Instron 3000*. The obtained data are monitored and processed using *Instron Bluehill Lite Material Testing Software*.

Evaluation of Wear Resistance

Wear resistance is fixed if at least one thread is damaged [24]. The *SDL Atlas M235 Martindale* machine was used with cloth samples. Sample (D=38 mm) was fixed in the sample holder, standard wool worsted fabric (D=140 mm) was used as abrasive, pressure load was 595 ± 7 g, according to the nominal pressure of clothing and home textiles 9 kPa, which characterizes the conditions under which textiles are encountered in real world [25].

Air Permeability

The air permeability of the samples was evaluated by the air permeability coefficient, measuring the amount of air that passes through a 5 cm² sample area in a given time and at an air pressure difference on both sides of 30 Pa and 100 Pa. The test was performed with the *SDL Atlas Air Permeability* device according to standard [26]. For each sample, 10 measurements were taken at different locations.

Estimation of the Wetting Equilibrium Angle

The wetting angle of the samples was determined with the optical tensiometer *Theta Attension* using the drop method with an accuracy of ± 0.1 . The device automatically performs and records all measurements, recording droplet volume changes and the wetting angle. For each sample, 3–5 measurements were made at one-minute intervals.

Evaluation of Vapour Permeability and Thermal Resistance

For both tests, the *Permetest. Skin model* equipment was used. Thermal resistance was determined by dividing the temperature difference between the two sides of the test material by the unit of generated heat flow to the zone in the direction of the gradient. Thermal resistance, expressed in m²·K/W, characterizes the flow of dry warm air of textiles or composites in the used area in response to the uniformly applied temperature gradient (ISO 11092:2014) [27].

To measure heat resistance, the temperature of the device was set to $T_m = 35$ °C and the air ventilation speed $v_a = 1$ m/s, ensuring the air temperature in the laboratory $T_a = 20$ °C and the relative humidity within 65 %.

The device determines water vapour resistance in the range of 1–200 m²·Pa/W⁻¹ and relative water vapour permeability in the range of 0.5–100 %. Before testing, the device is calibrated with standardized cloths (ISO 11092:2014) [27]. The temperature of the device, T_m , and the air, T_a , was set to 35 °C and the relative humidity should be around 40 %.

2.6. Methods of Evaluation of Applied Coating

Analysis of Antibacterial Properties

The disk diffusion method or Kirby-Bauer method is a technique used to test the development of rapidly growing microorganisms and pathogens using opposite plates with agar-based nutrients (DIN EN ISO 20645). The modified and unmodified samples were incubated for 18–24 hours at a temperature of 37 ± 2 °C. The results are based on the zone of inhibition around the samples as well as the bacterial growth under the sample. The sample can be defined as antibacterial even if there is no inhibition zone and growth of microorganisms under the sample. Two cultures *Staphylococcus aureus* (ATCC 29213) and *Escherichia coli* (ATCC 25922) were used to determine the antibacterial properties of modified and unmodified textiles. The used samples had a 11 mm diameter. Six parallel measurements were provided for each culture.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis

Micrograms of the surface of the samples were taken with a scanning electron microscope (SEM) with *SEM Mira Tescan HF*. The chemical composition analysis of the samples was performed using the *SEM Mira Tescan HF with Oxford Inca X-sight EDX* detector.

Fourier Transform Infrared Spectroscopy (FTIR)

In the process of Fourier transform infrared spectroscopy, interferograms from the full spectrum of the light source are recorded and analysed. To obtain spectra with a certain level of reliability that meet the needs of research and control of the structure, technology, and functionalization of platinized knitted fabric with a mixed fibre composition, several changes have been made to the traditional approach:

- 1) in the spectral analysis, the numerical values of the absorption coefficients of the spectra of the unmodified and modified samples obtained during one session were transferred to the *EXCEL* technological environment, which makes it possible to evaluate the dispersion of the ordinates corresponding to the wave numbers and to determine the number of spectra necessary to ensure the average values within the permissible relative error;
- 2) the obtained spectra were subjected to normalization for further processing, which makes it possible to perform comparative analyses;
- 3) taking into account that on both sides of platinized knitwear, the dominant threads on the surface differ in terms of fibre composition and other properties, the spectra taken for each side of the knitwear contain valuable information about the structure of the relevant surface, chemical groups, absorption changes under the influence of the applied coating, allow to determine coverage intensity and track the impact of parameter changes;
- 4) to facilitate quick reading of the results on the horizontal axis, the wave numbers appear in increasing order, the *EXCEL* tools allow easy and accurate quantitative coordinate readings or quick estimation of the frequency ranges corresponding to the spikes;
- 5) the difference spectra allow quantitative assessment of the absorption changes caused by the coating, which is essential considering that the fluctuations of the chemical groups/bonds of the cotton cellulose and silicon sol overlap in almost the entire range of wave numbers; when joining synthetic threads, it is possible to trace the effectiveness of the modification on them.

The spectra of the samples were taken with the *Bruker Tensor II* spectrometer using the attenuated total reflection (ATR) method. Ten parallel measurements were performed in each set. Spectra processing was performed with the *SpectraGryph. Spectroscopy Software* online program. The crystal used is a diamond whose spectral range is 50.000–2.500 cm^{-1} , refractive index is $n = 9.000$, and the measurement depth at 45° is 1.66 μm .

The following stages of the research have been introduced in the study of the structure and properties of platinized knitted fabric:

- 1) both sides of the knit should be examined separately;
- 2) spectra processing is initially performed with the *SpectraGryph. Spectroscopy Software* online program;
- 3) processing of spectra is transferred to the technological environment of EXCEL;
- 4) the number of spectra to be recorded is determined so that the recording error does not exceed 5 %;
- 5) performs normalization of the average spectrum of each set;
- 6) creates the combinations of spectra required for analysis and their comparative analysis;
- 7) creates difference spectra and performs their interpretation.

3. RESULTS

3. Modification of Knitted Products of Mixed Fibre Composition

Traditionally, T-shirts and hosiery products are made using cross-knit [28] knitted weaves, made of cotton yarn or combined with synthetic polyamide and/or polyester and elastane yarns. The mixed fibre yarns are combined to provide the necessary wearing comfort in contact with skin (provided by 75–80 % cotton yarn), abrasion resistance (provided by 18–20 % polyamide or polyester yarns), and elasticity (provided by 3–5 % elastane yarns).

By connecting different yarns in the knitting process and adjusting their tension ratio, a platinized knitted fabric is obtained, as it is important to ensure the intended functional properties: on the surface that is in contact with skin during the wearing process, there are mostly stitch circles (H) made of modified cotton threads, on the outer surface, mostly polyamide or/and polyester and elastane combined thread stitch posts (L) (Fig. 3.1), ensuring the required level of abrasion resistance

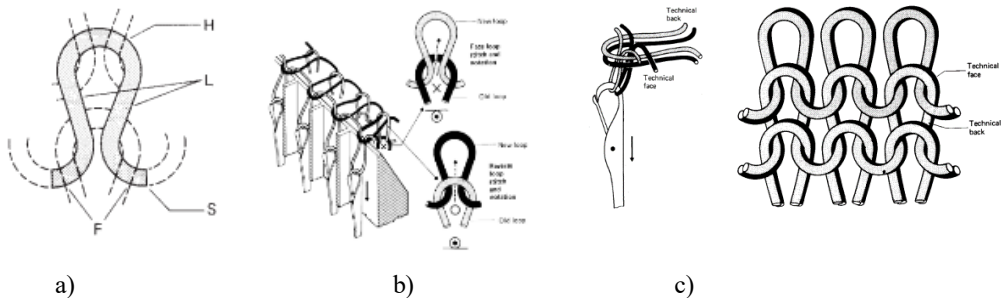


Fig. 3.1. Development of criss-cross plated knitted fabric on a circular knitting machine: a) intermeshing points of a needle loop; b) face- and reverse-meshed loops; c) plated knit loop and surfaces formation [28].

Characteristics of Cotton/PA Sock Products and Design of Experiments

Plain weave industrial cross-knitted socks with the composition of 81% ecologically grown cotton (CO) and 19 % polyamide (PA) were tested. The average density of loops in an area of 10 cm² is 100 loops in the vertical direction and 90 loops in the horizontal direction. Taking into account that the sock products of this assortment are intended to be worn in the warmest months of the year and are therefore regularly subjected to hydrothermal (HT) treatment, the purpose of the functionalization is to ensure the self-cleaning ability of the surface, thus reducing the severity of the HT treatment and increasing the intervals, while at the same time insignificantly reducing the wear comfort-providing features of the product. This type of functionalization is especially important in products with an integrated wearable electronics system, considering that the performance of the system elements decreases rapidly with each HT processing cycle and their failures occur well before the end of the physical life of the sock product.

For the solution of the problem, plan 2³ of the full factorial design experiment (PFE) [21] for the optimization of the final part of the sol gel process includes the heating time (x^1), temperature (x^2), and adding the concentration of the modifying precursor ZAD in the sol as the third investigated variable (x^3) was planned and executed. The intervals and levels of variation of all three factors were chosen based on the 100 % cotton fabric established in previous studies and are shown in the full factorial experiment's Plan 2³ (Tab. 3.1).

Table 3.1.

Full Factor Design Plan 2³

FACTOR DESIGNATION	FACTORS	CODED FACTOR LEVELS			VARIATION INTERVAL
		-1	0	1	
X ₁	Heat treatment time, min	5	6.5	8	1.5
X ₂	Heat treatment temperature, °C	100	110	120	10
X ₃	Zinc acetate dihydrate ZAD concentration, wt.%	5	6.25	7.5	1.25

Microstructures of the Fibre Surface of the Modified Knit

Comparing the SEM micrographs of the samples after the modification and the HT treatment at the end of the process, after the modification with 5 wt.% ZAD sol, three-dimensional agglomerates of partially reacted sol with a relatively weak connection to the surface, as well as some strands of stuck fibres can be observed on the fibre surface coating (Fig. 3.2 a)).

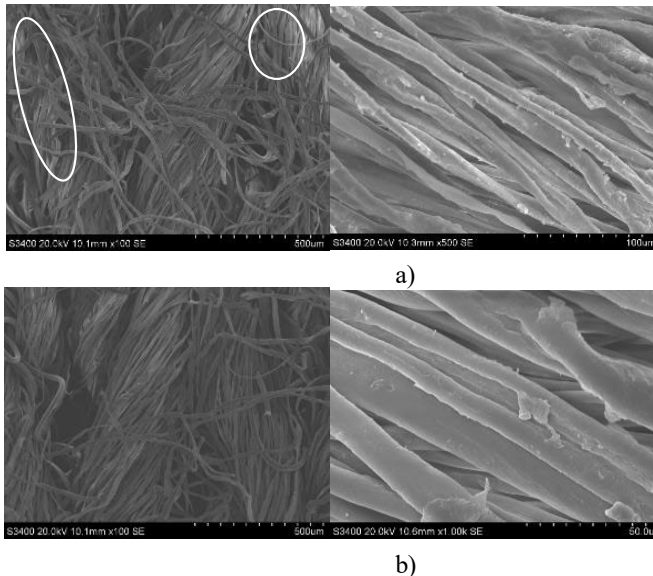


Fig. 3.2. Micrographs of the samples treated with 5 wt.% ZAD modified sol: a) after treatment with sol (120 °C; 8 min); b) after sol treatment (120 °C; 8 min) and HT treatment.

In the process of HT processing, in the presence of a large amount of water, the consolidation of the coating with the surface of the fibres continues; as a result, the strands of stuck fibres are not visible in the micrographs (Fig. 3.2 b) left), the coatings on the surface of the fibres have been smoothed, a few agglomerates stuck together in larger formations remain (Fig. 3.2 b) right).

Comparative Analysis of ATR-FTIR Spectra

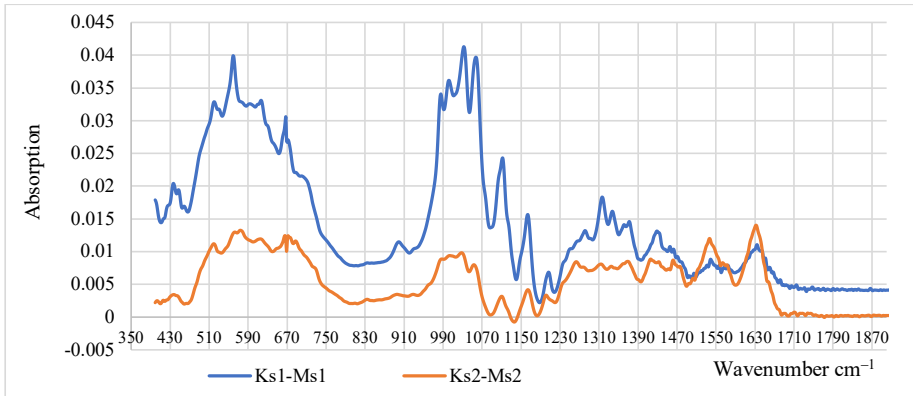


Fig. 3.3. Comparative absorption difference spectra of cotton/polyamide sock products.

In Fig. 3.3, the displayed CO/PA difference spectra allow to gain an insight into the distribution of absorption peaks of the coating as a result of the knitted surface modification and allow the identification of the chemical groups formed in the coating composition, which is difficult, taking into account that the sol-gel process does not proceed to the end due to the limited heating temperatures, as this is when heating is allowed at 600 °C and above. The spectra of the sol used in the [17] to show the characteristic peaks of the chemical groups of the sol in the frequency band 400–1650 cm^{-1} and 2900–3600 cm^{-1} when the heating temperature is 100 and 120 °C and allow the identification of the absorption intensity of the coating chemical group in the frequency bands corresponding to the peaks. Considering that the thickness of the coating is on average ~ 60 nm but the absorption measurements include $a \sim 1.7$ mm thick layer, the difference spectra show changes in the intensity of the substrate affected by the coating on the inner surface of the platinized structure (Ks1-Ms1), which characterizes a relatively large decrease in intensity in the bands of wave numbers corresponding to the chemical groups of cotton and a very small one in those characteristic of PA. On the other hand, the Ks2-Ms2 difference spectrum of the outer surface shows a decrease in absorption intensity under the influence of the modifying coating on the characteristic peaks of PA at 1537 cm^{-1} and 1632 cm^{-1} . Thus, the difference spectra can serve, among other things, to identify the presence of a coating on the filament fibres and to track what happens in the following processes (HT treatment, wear).

Comparative Analysis of Surface Wettability

To ensure the “easy care” effect, the surface ability of hydrophilic fibre textiles must be increased in the modification process to repel moisture (surface wetting angle $> 90^\circ$), while at the same time, maintaining the hydrophilic nature of the rest of the layer necessary for wearing comfort. Performing a comparative analysis of the wettability of the surface of the modified

sock product variants after modification with 5 wt.% ZAD sol (Fig. 3.4 a)), the heating temperature of 120 °C does not provide a stable expected effect, in contrast to the heating regimes suitable for this sol at 120 °C.

On the other hand, after the first HT processing cycle, the MM5-100/5 variant (Fig. 3.4 b)) shows a rapid drop in the average wetting angle from 161.12° to 114 ± 2°, but it stabilizes at this level after 60 s.

The surface of the heated socks at a temperature of 120 °C and after HT treatment is uniformly hydrophobic, showing the lowest wettability when the heating time has been 5 min. By increasing the heating time to 8 min, and maintaining the temperature at 120 °C, the wetting equilibrium angle decreases to 120 °C (Fig. 3.4 b). The most stable measurements are for samples MM5-120/5, where the post-treatment heating mode is 120 °C. The wetting angle remains stable during the entire measurement time, changing by 8 ± 2° (Figs. 3.4 a and b).

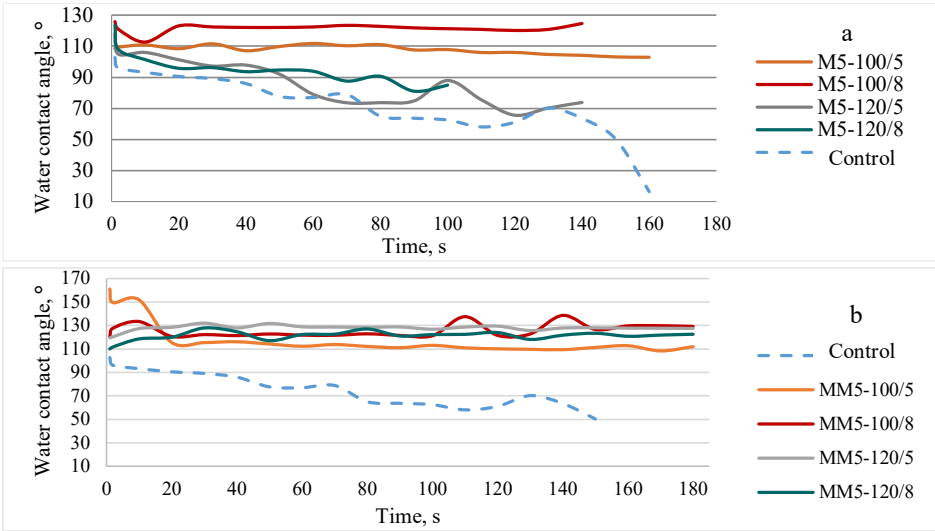


Fig. 3.4. Comparative analysis of surface wettability of 5wt.% ZAD sol-modified samples: a) before HT treatment; b) after HT treatment.

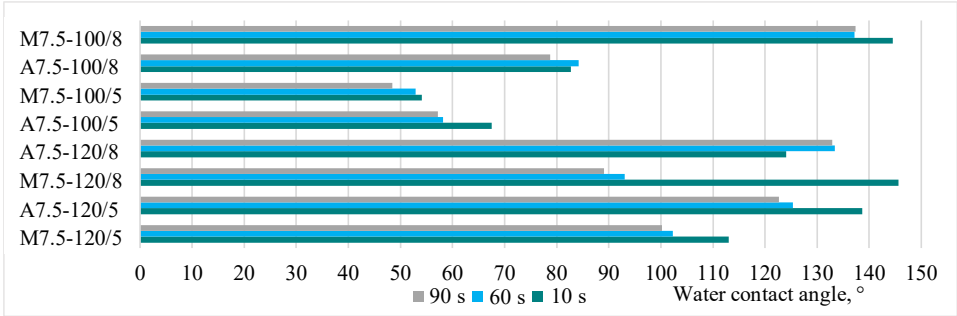


Fig. 3.5. Comparative analysis of surface wettability of samples modified with 7.5 wt.% ZAD.

After modification with 7.5 wt.% ZAD, the surfaces of samples soaked in acetone/water before modification (50 % acetone solution/5min) wet more than those only washed (Fig. 3.5). This trend is observed for all samples treated in acetone. The most stable readings are for sample M7.5-120/8, whose droplet equilibrium angle from the moment of filling (Figs. 3.6 a and b) to 60 s remains above 120°, changing by $\pm 10^\circ$.

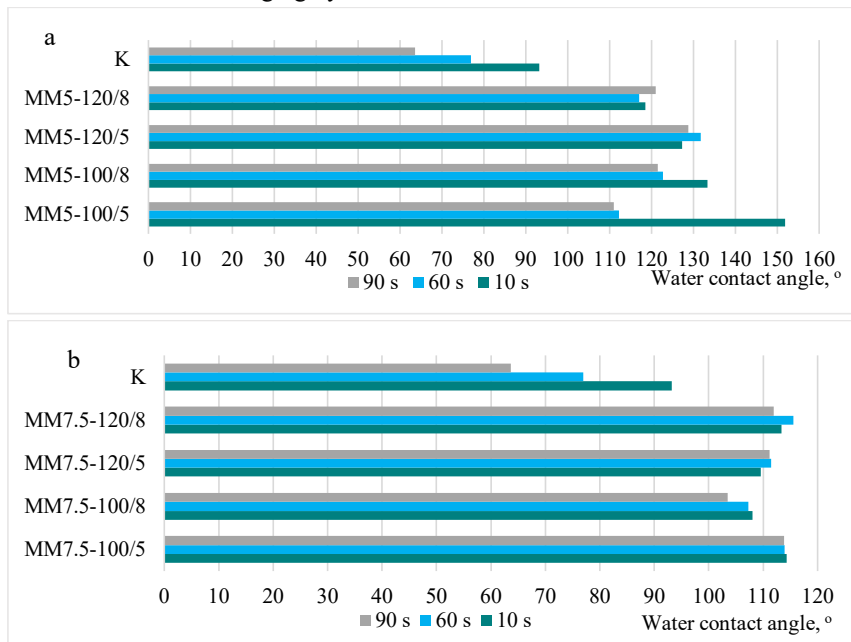


Fig. 3.6. Comparative analysis of surface wettability of ZAD sol modified samples: a) with 5 wt.% and b) 7.5 mass.%.

In general, comparing the effect of the ZAD concentration of the sol modifier, it can be concluded that a higher hydrophobicity effect (wetting angle within 110–130°) of the CO/PA knitted surface can be achieved with a 5wt.% ZAD content in sol. Increasing the ZAD content to 7.5 mas.%, the wettability of the surface increases (the wetting angle decreases to 100–115°), probably due to the decrease in surface porosity as the thickness of the coating increases.

Evaluation of Antibacterial Activity

Using the disk diffusion method, the antibacterial efficiency of modified textiles was studied against 2 reference cultures: gram-positive *Staphylococcus aureus* ATTC 2913 and gram-negative *Escherichia coli* ATCC 25922. Antibacterial efficiency was determined by evaluating the intensity of growth above and below the sample, as well as the diameter of the inhibition zone.

With 7.5 wt.% ZAD precursor sol modified platinized plain weave cross-knitted (CO81 % / PA19 %) samples, a pronounced antibacterial effect was observed against both tested microorganisms (Fig. 3.7) if the hydrofluoric acid was used as a catalyst in the sol synthesis. Attempts to replace HF with the more environmentally friendly acetic acid, made within the framework of the Thesis, unfortunately did not provide the expected intensity of the

antibacterial effect. Perhaps, in future research, we should try to find another, more environmentally friendly medium strong acid. For example, it could be formic acid, but the question is whether a sol with formic acid in its composition can be used for the functional modification of textiles containing PA fibres because PA is soluble in this acid.

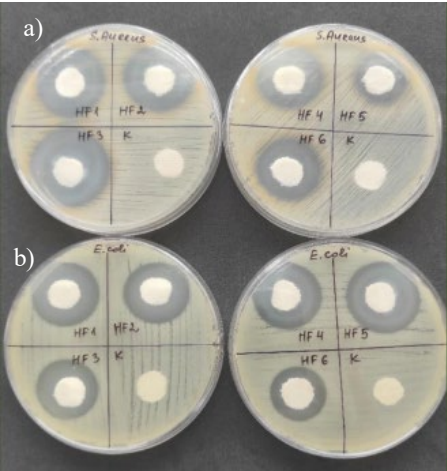


Fig. 3.7. Antibacterial activity of modified (HF) and unmodified samples against a) *Staphylococcus aureus* ATCC 2913 and b) *Escherichia coli* ATCC 25922*.

*Sample unmodified knit on quadrant 4 of each disc.

Comparative Analysis of Air Permeability

Air permeability (AP) measurements of hosiery products were performed in one layer at 10 locations. The pressure was reduced from the standard 50 Pa, considering that the density of the knitted fabric is low, therefore the GC was so high that the measurements at this pressure were outside the scale of the machine.

After modifying the samples with 5 wt.% ZAD concentration of the sol solution and the subsequent HT treatment, the observed air permeability decreases on average in the sock stump from 26 % to 38%, and in the foot from 19 % to 28 % (Table 3.2). Since the foot is the part of the sock product that is in an unfavourable environment during the wearing process, the heating modes of 8 minutes at 100 °C and 120 °C provide the lowest AP reduction in the modified foot part.

Table 3.2

Socks Treated with 5 wt.% Comparative AP of ZAD Modified Sol, mm/s

X ₁	X ₂	Leg		Foot		Modification effect		Washing effects		Non-modif.	
		M5	MM5	M5	MM5	Leg	Foot	Leg	Foot	Leg	Foot
5	100	587	494	439	565	26.7 %	44.4 %	16 %	29 %	38 %	28 %
8	100	626	494	604	582	21.9 %	23.6 %	21 %	4 %	38 %	26 %
5	120	593	543	527	642	26.0 %	33.3 %	8 %	22 %	32 %	19 %
8	120	681	593	620	576	15.1 %	21.5 %	13 %	7 %	26 %	27 %
Control		801.4		790.53							

After modification of the samples with 7.5 wt.% ZAD concentration of the sol solution and subsequent HT treatment, AP decreases from 20–23 % were observed on average in the sock, while in the foot it was a little more – from 22–28 % (Table 3.3), considering the denser knit structure in the foot. To ensure a smaller reduction in permeability, when modifying with 7.5 wt.% ZAD, the heating time should be 8 min at 100 °C and 5 min at a temperature of 120 °C.

Table 3.3

Socks Treated with 7.5 wt.% Comparative AP of ZAD Modified Sol, mm/s

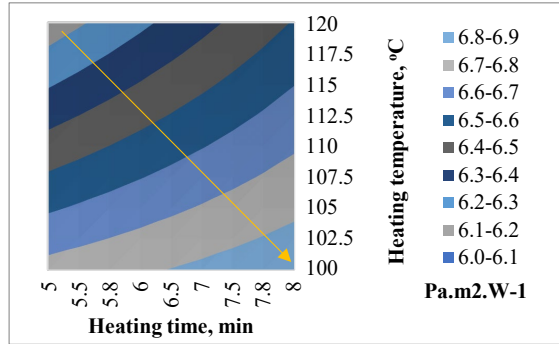
x_1	x_2	Leg		Foot		Modification effect		Washing effect		Non-modif.	
		M7.5	MM7.5	M7.5	MM7.5	Leg	Foot	Leg	Foot	Leg	Foot
5	100	758	620	747	571	5.5 %	5.6 %	18 %	24 %	23 %	28 %
8	100	637	615	626	598	20.5 %	20.8 %	3 %	4 %	23 %	24 %
5	120	703	642	681	615	12.3 %	13.9 %	9 %	10 %	20 %	22 %
8	120	758	637	714	587	5.5 %	9.7 %	16 %	18 %	21 %	26 %
Control		801.4		790.53							

Analysis of Water Vapour Permeability

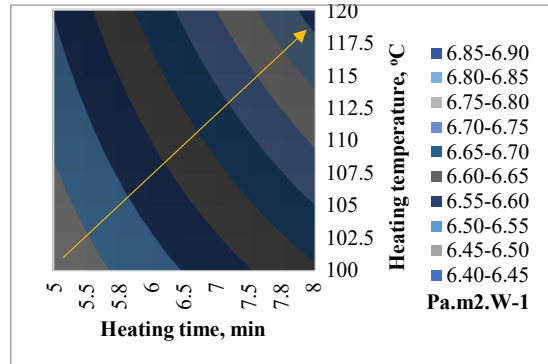
The obtained regression Eqs. (3.12) and (3.13) and their corresponding two-dimensional contour plots (Fig. 3.8) allow us to conclude:

- WVP of products modified with 5 wt.% ZAD sol is preserved better if they are subjected to HT treatment before modification; within the examined limits of heating time and temperature, WVP remains better if a longer processing time (8 min) is combined with a lower heating temperature (100 °C).
- The samples modified with 7.5 wt.% ZAD sol provide the best vapour permeability when applying 8 min of long-term heating and maintaining the temperature at 120 °C.

In general, HT pre-treatment is sufficient, as shown by the results. On the other hand, pre-treatment with acetone solution has a negative effect on the results (AP and WVP measurements).



a) $YTMM1 = 6.56 + 0.13 x_1 - 0.24 x_2 + 0.06 x_1 x_2$ (3.1)



b) $YTMM2 = 6.63 + 0.13 x_1 + 0.08 x_2 + 0.03 x_1 x_2$ (3.2)

Fig. 3.8. Measurements of water vapour permeability after HT treatment of the samples modified with a) 5 wt.% ZAD and b) 7.5 wt.% ZAD sol.

VP of the products modified with 5 wt.% ZAD sol is preserved better if they are subjected to HT treatment before modification; within the examined limits of heating time and temperature, VP remains better if a longer processing time (8 min) is combined with a lower heating temperature (100 °C).

In the case of samples modified with 7.5 wt.% ZAD sol, combining 120 °C and 8 min ensures better water vapour permeability.

Thermal Resistance Analysis

The samples treated with 7.5 wt.% ZAD sol have a 31 % higher thermal resistance than the samples treated with 5 wt.% ZAD concentration (Fig. 3.9). After washing, the thermal resistance decreases compared to the corresponding indicator before washing. These changes should be attributed to the changes in the structure of the coating and the strengthening of the surface adhesion during the HT treatment process.

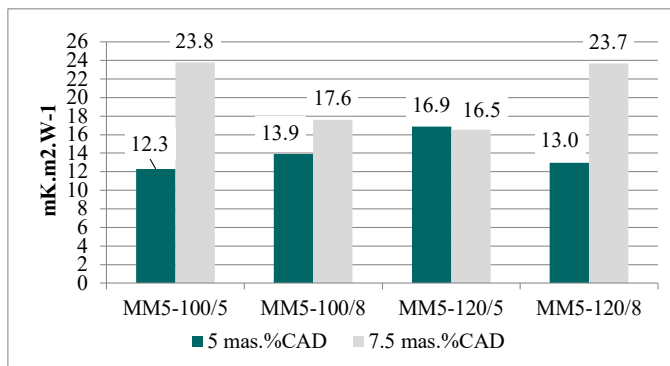


Fig. 3.9. Thermal resistance of 5 wt.% ZAD and 7.5wt.%ZAD for sol-modified samples after HT treatment.

Summary and Conclusions of Chapter 3

1. Industrial cross-knitted mixed fibre composition (81 % CO, 19 % PA) stocking products modified with TEOS precursor sol by integrating zinc acetate dihydrate as a modifying precursor with the aim of giving additional functional properties to improve product performance while at the same time maintaining user comfort, as well as to optimize the technological parameters of the sol-gel process for ensuring the properties of the modifying coating on the fibre surface of the knitted substrate of mixed fibre composition.
2. By varying the heating time of the final part of the modification, the temperature, and the ZAD concentration of the modifying precursor in the sol according to the full factorial experiment Plan 2³ and by comparing the surface properties of the modified and unmodified knits, it was concluded:
 - SEM micrographs show that after the modification, three-dimensional agglomerates weakly connected to the coating can be observed on the fibre surface, as well as clumped fibres. In the following hydrothermal treatment process, the coating is consolidated with the fibre surface, forming a uniform cross-linked nano-scale coating with a rough surface structure, providing hydrophobic surface properties: within 110–130° using 5 wt.% ZAD concentration.
 - An comparative analysis of ATR-FTIR spectra shows that the applied modifying coating is on both cotton and PA fibres (peaks at 1538 cm⁻¹ and 1634 cm⁻¹), as there is a reduced intensity of absorption in the frequency bands 400–700 cm⁻¹, 950–1150 cm⁻¹, 2850–2952 cm⁻¹, and 3170–3470 cm⁻¹, and allows tracking the intensity of changes, as well as identifying the functional chemical groups of the coating, considering that due to the limited heating temperature, the coating obtained in the sol-gel process has an amorphous structure and it is difficult to identify the chemical compounds in it.

- The comparative analysis of the difference spectra shows that due to the coating obtained as a result of the modification, the absorption intensity of the chemical bonds of the surface of the CO/PA knitted surface structure becomes weaker on both sides of the knitted fabric in almost the entire range of wave numbers (400–4000 cm^{-1}) and can serve as a control tool for platinized in the process of obtaining the structure of the knit and in the process of applying the coating to achieve the expected properties.
3. As a result of the comparative analysis of the wettability properties of the surface, it was found:
- Pre-treatment of hydrothermal samples is preferable to treatment of cleaning the surface of knitted samples with an acetone solution, because the hydrothermally treated samples after modification and hydrothermal post-treatment provide values of the wetting equilibrium angle of at least 110° , in three variants it exceeds 120° (ZAD 5 wt.%), which means that the modified surfaces are classified as hydrophobic. On the other hand, the wetting equilibrium angle of samples treated with acetone does not exceed 90° or is unstable – the applied coating does not provide the surface with water-repellent properties.
 - The wetting equilibrium angle values are more influenced by the interaction of heating temperature, heating time and ZAD concentration. In general, a higher hydrophobicity can be achieved with a 5 wt.% ZAD concentration by combining a higher heating temperature with a shorter time.
4. The antibacterial efficiency of the modified textiles against the reference cultures – Gram-positive *Staphylococcus aureus* ATTC 2913 and Gram-negative *Escherichia coli* ATCC 25922, determined by the disk diffusion method, can be considered:
- as high, as for the samples with hydrofluoric acid in the composition of the modifying sol, the average zone of inhibition is 27 mm and 26 mm, respectively;
 - replacement of hydrofluoric acid with acetic acid should be considered ineffective if the antibacterial activity of the sock product is expected to be ensured as a result of the functionalization.
5. A comparative analysis of the features characterizing the wearing comfort shows:
- Air permeability after modification with a 5 wt.% ZAD in the sol and the first hydrothermal treatment sock product decreases by 26–38 % and in the foot from 19–28 %; after modification with a 7.5 wt.% ZAD, the reduction in the sole is 20–23 % and in the leg from 22–28 %. In both cases, the air permeability of the modified hosiery products is significantly higher than that of woven fabrics with a similar surface density.
 - The highest air permeability (681 mm/s) for the position of the considered assortment can be ensured by modifying with a 5 wt.% ZAD bench and combining the heating temperature of $119\text{--}120^\circ\text{C}$ with the processing time within 7.8–8 min.
 - After the final hydrothermal treatment, as the coating consolidates, the air permeability values move to a lower interval within the range of 494–593 mm/s.

- Combining a heating temperature of 100–105 °C with a time of 7–8 min can ensure a reduction of air permeability after hydrothermal treatment within the limits of only 10 % compared to the control sample.
6. The following investigation of the mathematical model of the equations (2D contour plot) allows to obtain detailed information about the influence of all three factors on the comfort-providing properties of the samples, such as vapour permeability and thermal resistance, and conclude:
- The vapour permeability of the samples modified with a 5 wt.% ZAD remains better if they have been hydrothermally treated before the modification, if a longer treatment time and a lower temperature (8 min/110 °C) are combined.
 - On the other hand, with the 7.5 wt.% ZAD, the trend is opposite: similar results can be achieved by applying a temperature of 120 °C and a heating time of \pm 8 min.

In general, the proposed technological solutions allow to modify industrially knitted cotton/PA and cotton/PES platinized plain knit sock products to give functional properties while maintaining the comfort-providing properties.

4. Technology for the Development of Knitwear with Integrated Modified Cotton Yarn

The solution proposed in the Doctoral Thesis envisages dividing the acquisition of modified knitwear into two consecutive processes: 1) modification of cotton yarn to give functional properties; 2) preparation of the modified yarn for knitting and designing of the knitting process by integrating the modified yarn with unmodified polyamide/polyester and elastane threads on the knitting machines, if necessary, with the intention of including subroutines for inserting sensors and electroconductive threads into the control program of the knitting machine.

Modification of Cotton Yarn

The process of obtaining the modified cotton yarn is divided into ten steps (Fig. 4.1), providing for the intensive cleaning of the industrially obtained yarn from the natural coating of cotton fibres, the cycles introduced in the technological process of obtaining the yarn, passing it in a climatic chamber to ensure a controlled moisture content, synthesis of the sol solution to ensure the expected functional properties, yarn modification as the last, providing mandatory HT treatment to conclude the coating consolidation process.

Preparation of Yarn for Modification

Industrially produced 100 % cotton worsted yarn (linear density 24 tex) is rewound from the cross bobbins onto the wicks to ensure free circulation of the modifying solution during the processing. Before soaking in the sol solution, the threads wrapped in fices are divided into strands, they are tied at regular intervals with loose ties to protect the threads from sticking together during the modification process, followed by pre-treatment at 100 °C, drying and relaxation in the climatic chamber (Fig. 4.1, Steps 1–3).

Yarn Modification in the Sol–Gel Process

The prepared yarn fibres are subjected to processing in the sol–gel process by applying the sol composition and technology to it, varying the ZAD content and immersion time in the sol, as well as the temperature and duration of the thermal post-treatment (Fig. 4.1, Steps 4–10). For technology approval, the 7.5 wt.% ZAD precursor sol was used by varying the proportion (sample weight (g) against the amount of solution (ml)), immersion time in it, maintaining a

fixed thermal post-treatment temperature of 120 °C and a time of 5 min. The choice of variable and fixed parameters is based on the results of the research presented in Chapter 3.

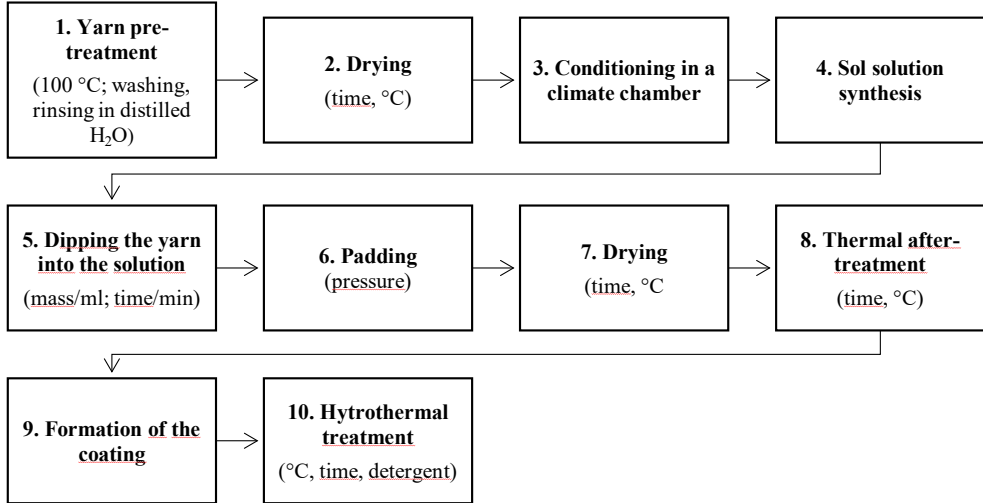


Fig. 4.1. 10. Technological sequence of cotton yarn modification [29].

Development of Knitwear with Integrated Modified Yarn Component

In the process of preparing the modified yarn for knitting, the yarn is rewound from the skeins to a suitable package for the knitting machine/machine, in most cases using a cross winding on conical shells (Fig. 4.2, Step 4). If necessary, yarn waxing, or emulsification is integrated into the rewinding process to facilitate the stitch formation process while knitting.

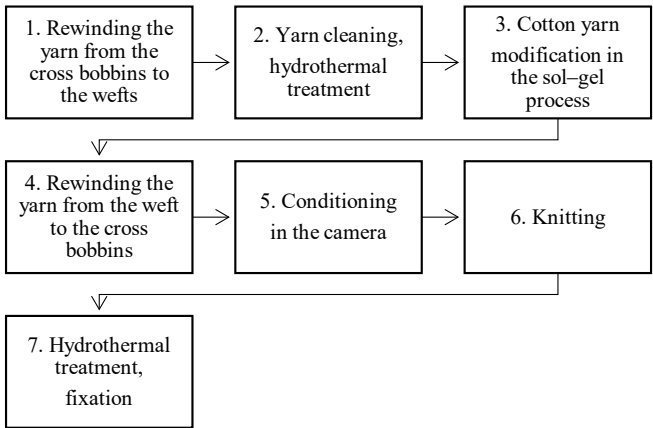


Fig. 4.2. Block diagram of producing knitted products with an integrated modified yarn component [29].

Before knitting, the yarn must be kept in the climatic chamber for at least 24 hours. In the 6th operation (Fig. 4.2), all the intended thread components, including the modified cotton yarn, enter the bobbin holders of the knitting machine and are fed to the knitting zones through separate yarn guides with the necessary tension according to the commands of the production control program. Thus, the modified yarn in rows 5–7 can be included in the traditional programs of the knitting machines of the relevant class and the final hydrothermal treatment modes.

Investigation of Applied Modifying Yarn Coating

Taking into account that the so far developed sol–gel technology [17] was developed for the modification of cotton fabrics, the application of the technology to yarn that is not stressed during the processing process and thus exposed to uncontrolled deformations, as well as the fact that the access of the modifying sol to the entire surface area of the yarn is practically not limited, it is necessary to control changes in the stability of technological parameters of the modification, the volume and properties of the applied composition, which affect the progress of the technological process of knitting.

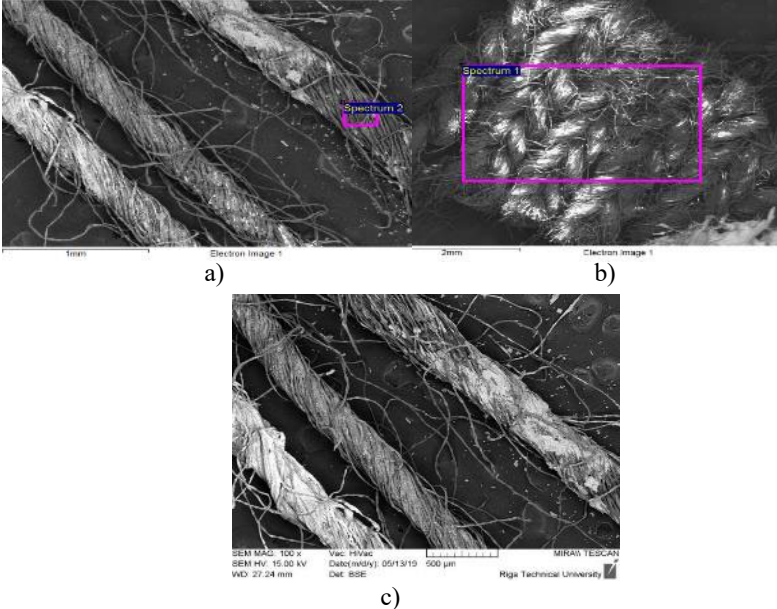


Fig. 4.3. Selection of location and size of testing areas; a) modified yarns, b) knitted sample of modified and HT treated yarn; c) modified yarn (M/1:10/10).

SEM analysis to analyse the structure of the coating applied during the modification process. Agglomerates that stand out on the surface are often of interest to identify their composition. When trying to study them, the selected area is very small (Fig. 4.3 a)), thus there is a large scatter in determining the true distribution of elements on the surface and erroneous conclusions about their relative distribution. To evaluate it, a larger area should be selected (Fig. 4.3 b)). On the other hand, repeated measurements make it possible to clarify that the agglomerates on the background of the coating are formed by partially/undissolved particles of

Zn acetate at the nano- and micro-level, where the relative Zn content in spot measurements can reach up to 20 wt.% (Table 4.1).

During the modification process, due to the uneven precipitation of the sol solution and the surface of the yarn filaments, thickening of the applied coating may occur, which due to the insufficient amount of available water, does not completely transform into a xerogel during the heating process (Fig. 4.3 c) due to the formation of clusters of stuck fibres.

The percentage ratios describing the relative occurrence of elements, compiled in Table 4.1, allow tracking the occurrence of elements on the modified surface and their mutual proportions. Along with modifying elements F, Si, and Zn, elements have been found which, despite careful yarn cleaning, remain on the fibres from previous technology finishes, as well as come from impurities of standard washing powder (Na, Cl, As) and water used in the process.

Table. 4.1

Relative wt.% of Chemical Elements Found on the Surface of Sample (M/1:10/10)
in EDX Analysis

Designation	C	O	F	Si	Zn	Ca	Al	S	Mg	Na	Cl	Cu	As
“2304 Standard Sope” wash remedy	71.4	21.4								6.7	0.2		0.3
Unmodified threads, 24 tex	47.0	52.3	-	-	-	-	0.1	0.3	-	0.3	-	-	
Modified threads, 24 tex	34.9	35.2	7.6	1.3	18.0	-	-	0.2	0.1	-	1.9	-	
Modified HT threds, tex	47.6	47.2	2.5	0.5	0.7	0.9	0.1	0.6	0.1	-	-	0.1	
Knitwear with modified yarn, HT	47.1	46.5	3.2	1.0	0.8	1.1		0.2	0.1				

In the HT treatment process, Ca was found in the coating from the used water, while Al or Cu appear if they come into contact with the foil or with the respective metal sample holder during the sample drying process. As a result, after the HT treatment following the modification, the coating has stabilized, forming a close bond with the surface of the fibres, and in the subsequent technological operations, the relative content of the elements providing the functional properties – F, Si, and Zn – is relatively stable, as shown in the last 2 rows in Table 4.1 [30].

Comparative Analysis of the Properties of Modified and Unmodified Cotton Yarn

A device was used for testing the modified yarn, which simultaneously allowed to record such parameters characterizing the properties of the yarn as breaking load, elongation, tensile stress at maximum load, as well as the mass of the corresponding sample.

The composition of the sol was fixed using the ZAD concentration of the sol modifier at 7.5 % by mass. As shown in Table 4.2, the data processing results compiled in the Table and Fig. 4.5, the mass of the modified yarn increases compared to the unmodified depending on the soaking parameters in the range of 1.4–5.1 wt.%, the tensile deformation can decrease up to 25 %, but the tensile strength increases in the range of 23–47 %, reaching the maximum value at the ratio 1 : 10 and soaking time 10 min.

Table. 4.2

Changes in cotton yarn properties under the influence of modification parameters

Variant	Linear density, tex		Mass increase, %	Tensile strain, %		Tensile strain decrease, %	Tensile strength, cN/tex		Tensile strength increase, %
	Avg.	-/+		Avg.	-/+		Avg.	-/+	
Control	25.7	0.3		6.95	0.14		9.58	0.19	
M/W/1:12/15	26.07	0.22	1.44 %	5.76	0.12	17 %	13.47	0.19	41
M/W/1:12/5	26.59	0.24	3.46 %	6.92	0.12	1 %	12.83	0.19	34
M/W/1:10/10	27.01	0.23	5.10 %	6.50	0.12	7 %	14.08	0.20	47
M/W/1:8/5	26.73	0.23	4.01 %	6.43	0.11	7 %	13.46	0.19	41
M/W/1:8/15	26.05	0.26	1.36 %	5.21	0.15	25 %	11.76	0.27	23

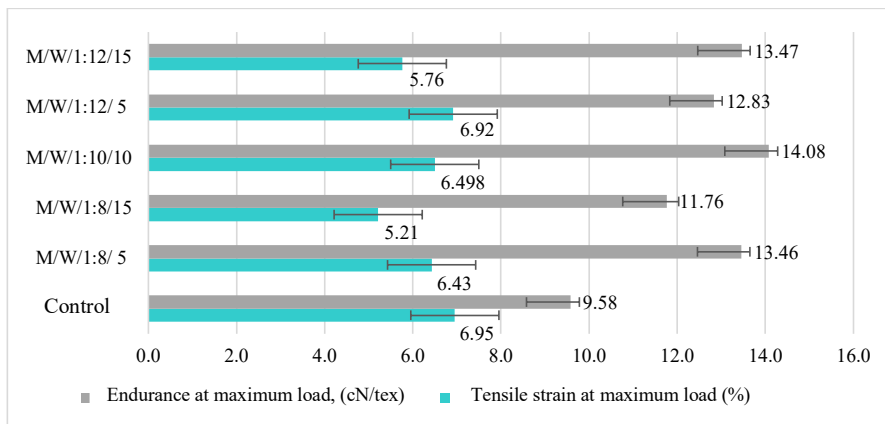
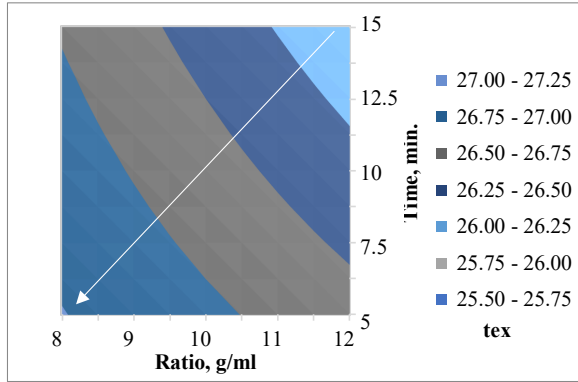


Fig. 4.4. Tensile strength (cN/tex) and the percentage of tensile strain (%) of unmodified and modified yarn at maximum load.

Changes in the linear density (Y_{LB}) of the modified yarn depending on the sample's mass-sol volume ratio (x_1) and the immersion time in the sol solution (x_2) are described by Eq. (4.1) and the corresponding surface slices (Fig. 4.5).

Both the coefficients of the equation and their signs, but especially the graphical interpretation of the equation, show that the maximum percentage increase in linear density corresponds to the combination of a ratio of 1 : 8 and a soaking time of 5 min (indicated by the arrow in Fig. 4.5). Moving along the arrow upwards, the increase gradually decreases, reaching the minimum value corresponding to the combination – ratio 1 : 12 and immersion time 15 min.



$$Y_{LB} = 26.60 - 0.27x_1 - 0.20x_2 - 0.06x_1x_2 \quad (4.1)$$

Fig. 4.5. Variation of the linear density of modified yarn depending on the ratio and the dipping time.

Parameters Characterizing the Structure of Cotton/PA/Elastane Knitted Fabrics

Samples of cross-knitted platinized plain weave cloths were made from modified and unmodified cotton yarn from the DMW_1-4 variant yarns in the knitting process by incorporating unmodified combined polyamide-elastane threads alongside the cotton yarn in ratio: 75 % cotton / 21% polyamide / 4 % elastane.

Table. 4.3

Structure Characteristics of Knitted Fabrics (75 % CO / 21% PA / 4 % elastane)

Characteristic parameter	Variant				
	K	MWT/1	MWT/2	MWT/3	MWT/4
Loop density in the horizontal direction, cm ⁻¹	9.5	9.8	9.8	10	10
Loop density in the vertical direction, cm ⁻¹	15	15.5	15	14.5	15.2
Total density, cm ⁻²	144	151	148	145	148

The values characteristic of knitted fabrics, compiled in Table 4.3, show that the total loop density of the modified samples has increased slightly (2.6 %), which is natural, considering the increase in the linear density of the cotton yarn after the modification. After the final HT treatment, the surface of the fibres in the threads has become smoother as the coating consolidates with the surface of the fibres, the diameter of the threads has increased, as a result, the knit has become denser at the same settings of the knitting machine.

Comparative Analysis of FTIR-ATR Spectra

The cotton yarn was impregnated with a 7.5 wt.% ZAD modifier bench, heated for 5 min at 120 °C, combined with textured polyamide/elastane threads into a knitted sock structure. Figure 4.5 shows the spectra of knits containing unmodified and modified cotton yarns.

The frequency bands of the modified samples with peaks at 1454.72 (CH₂ bend) and

1538 cm^{-1} (NH bend, C-N stretch), as well as at 2917.28 cm^{-1} and 2848 cm^{-1} (CH stretch) are attributed to the vibration frequencies of chemical groups characteristic of PA [31]–[34].

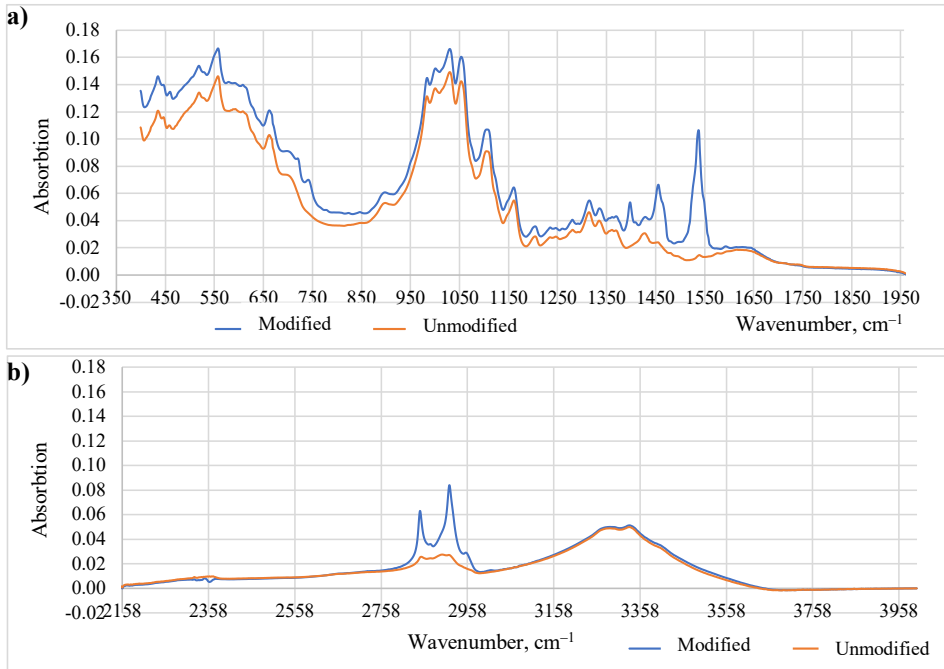


Fig. 4.6. Spectra of knitted samples containing modified and unmodified cotton yarns.

Comparative Analysis of Air and Water Vapour Permeability

As can be seen in Table 4.4, according to the test results summarized in the table, the AP of the knitted samples with the modified cotton yarn decreases by an average of 21 % (within the range of 17–24 %) compared to the AP of the unmodified yarn samples. This is a smaller reduction compared to the AP reduction of woven cloth samples ~2 times compared to the unmodified one (20 % on average) [30].

Table 4.4

AP and VP Results of Knitted Fabrics (75 % CO / 21 % PA / 4 % elastane)

	K	MWT/1	MWT/2	MWT/3	MWT/4	Avg.MWT
Air Permeability, mm/s	518.8	394.3	409.1	409.4	432.5	411.3
-/+ (mm/s)	13.9	24.0	11.2	14.8	28.4	21.89
Decrease, %	-	24 %	21 %	21 %	17 %	20.8 %
Relat. vapour permeability, %	49.4	47.0	53.0	48.2	48.1	49.1
-/+ (%)	9.0	0.6	3.2	1.6	3.7	
Decrease/increase, %	-	5 %	-7%	2 %	3 %	0.8 %

This can be explained by the inherent porosity of the knitted structure and the presence of textured unmodified polyamide yarns, which maintain the external porosity of the fabric by

compensating for the effect of the reduced porosity of the surface of the modified yarn. As the average residual AP of 411 mm/s exceeds 150 mm/s, the sock products containing modified yarns are suitable for wearers of all age groups from the 1–3 years age segment [35],[36]. Relatively insignificant is the decrease in relative VP, which does not exceed 5 % (on average 0.8 %). Considering that these two properties of the fabric are very important for ensuring wearing comfort, it can be considered that the technology proposed in the Thesis can provide wearing comfort much better than a fabric modified with a similar sol composition.

Abrasion Resistance

Figure 4.7 K(unmodified) shows that after 5.000 rubbing cycles, pronounced visual defects such as fraying and pilling have formed on the surface of the control cloth. At the same time, on the surface of the modified cotton yarn containing MWT/1 and MWT/2 variants, after 5000 cycles, only a small tufting is observed (Fig. 4.6, MWT/1 and MWT/2), but the peeling effect is not observed after 15.000 cycles (Fig. 4.7, MWT/1 and MWT/2), it can start to form after ~ 20.000 rubbing cycles. The increased wear resistance of the modified samples is due to the tighter attachment of the cotton yarn fibres, the smooth silicon-containing fibre surface coating, which consolidated after the final HT treatment. It is possible that as the linear density of the yarn increases during the functionalization process, the surface area that resists wear also increases.

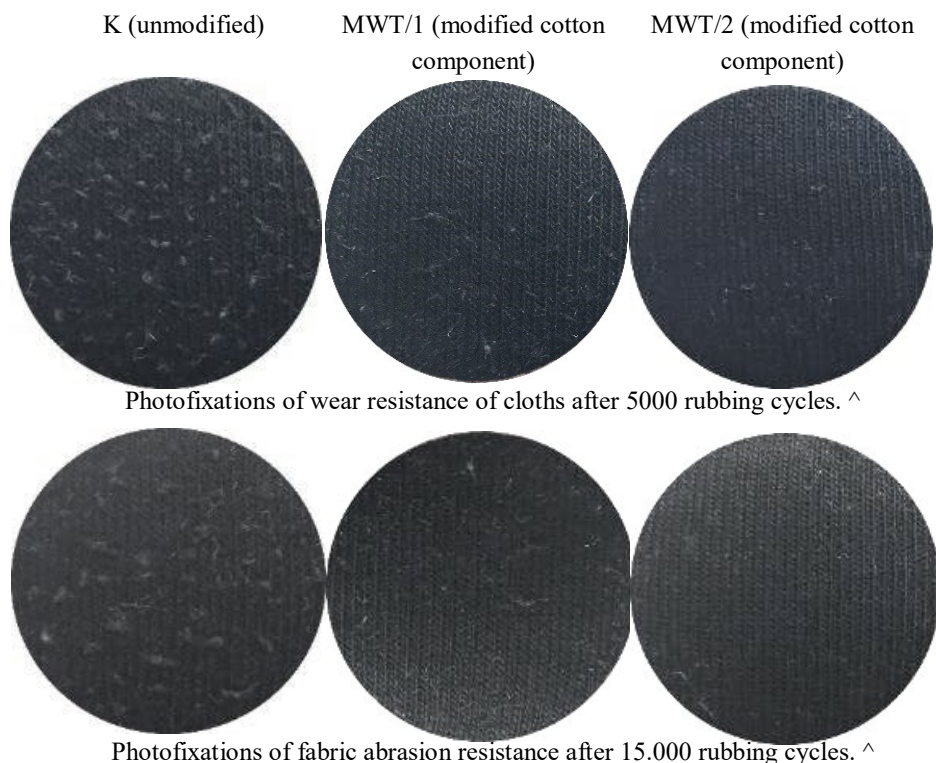


Fig. 4.7. Surface photo fixations of cotton/PA cloths after 5.000 and 15.000 rubbing cycles.

Characteristic Parameters of Modified Cotton and Polyester (PES) Knitted Fabrics

Unlike the previously discussed cotton/PA knitwear, in knitting with PES/elastane in the composition, the stitch density in the vertical direction varies between variants within the range of 2.7–10.2 % (Table 4.5), which also mainly affects the changes in the total stitch density.

Table 4.5

Structure Characteristics of Knitted Fabrics (75 % CO / 21 % PES / 4 % elastane)

Sample set	Characteristic quantities			
	Density in horizontal direction, cm ⁻¹	Density in vertical direction, cm ⁻¹	Total density, cm ⁻²	Increase in total density, %
Control	9.9	14.7	145	-
M/W/1:8/5	9.9(+0 %)	16.2(+11 %)	160.4	10.6 %
M/W/1:8/15	9.6(-4 %)	15.1(+3 %)	145	0 %
M/W/1:10/10	9.8(-1 %)	16.2(+11 %)	158.8	9.5 %
M/W/1:12/5	9.6(-4 %)	16.1(+10 %)	153.8	6.1 %
M/W/1:12/15	9.9(+0 %)	15.7(+7 %)	154.2	6.3 %

Comparative Analysis of FTIR-ATR spectra

Comparing the visible spectra of the KS2 variant in Fig. 4.7, it can be seen that the two spectra of the left side of the knitted fabric (KS1 and 2S1) are dominated by enhanced absorption zones in the wavenumber bands, corresponding to the chemical group characteristic of cotton.

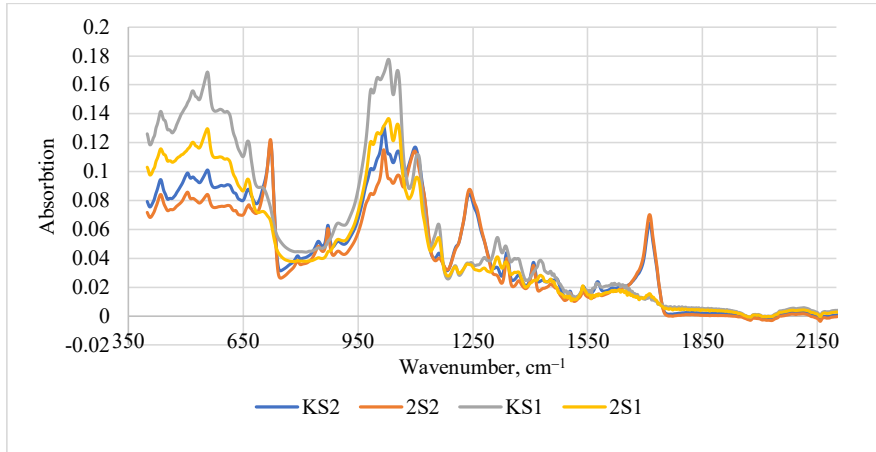


Fig. 4.8. MW/1:8/15 (ratio 1 : 8; time 15 min) comparative FTIR-ATR spectra of the left (cotton) side and the right (PES) side

In $400\text{--}680\text{ cm}^{-1}$ and $950\text{--}1124\text{ cm}^{-1}$, the decrease in the intensity of the absorption of the modifying coating is significantly greater due to the dominance of cotton threads that have been modified (Fig. 4.7, Spectra KS1, 2S1). On the other hand, for wave numbers 723 cm^{-1} , the peaks corresponding to 1246 cm^{-1} and 1713 cm^{-1} indicate the effect of platinumization in the formation of a good coating of PES threads on the outer surface of the knit (Spectra KS2 and 2S2) with a fragmentary appearance of the modified cotton threads, which is evidenced by the small change in absorption intensity in the spectra of the outer surface (the area between Spectra KS2 and 2S2).

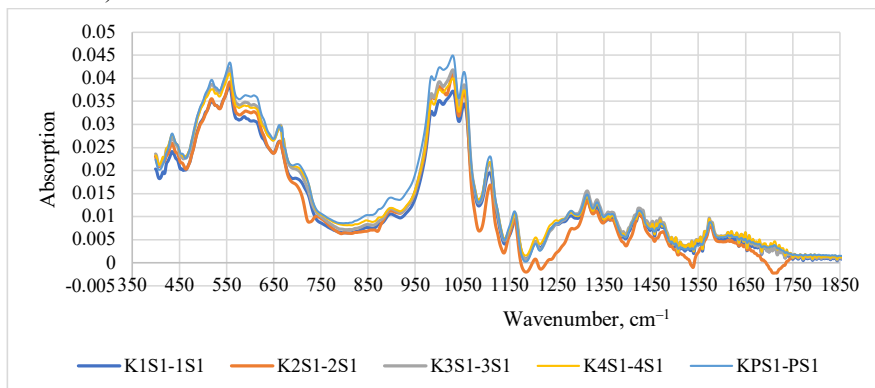


Fig. 4.9. Difference spectra of comparative cotton surface of variants.

Antibacterial Assessment

The antibacterial activity of the modified knitted fabric was observed against both test bacteria, which was characterized by an inhibition zone formed around the samples, especially pronounced for the *Staphylococcus aureus* clone, and no overgrowth with test bacteria was detected under and above the samples (composition CO/PES).

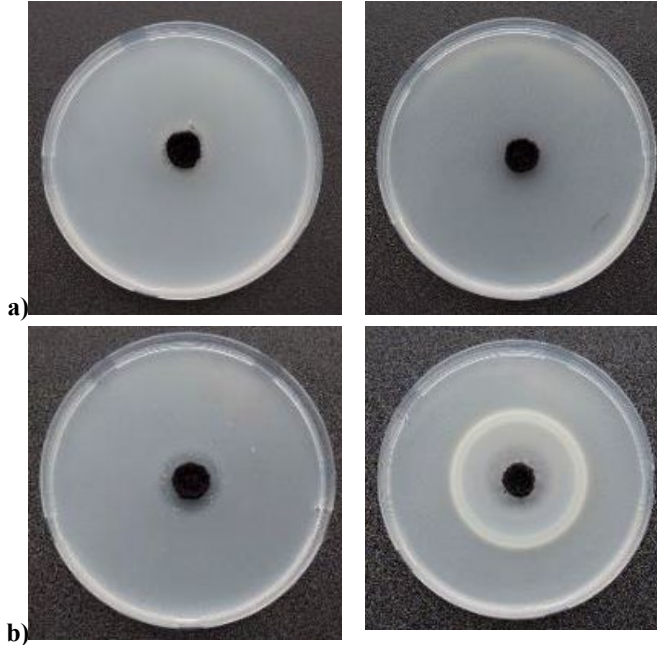


Fig. 4.10. **a)** Activity of unmodified knitted fabric samples against *Bacillus subtilis* mscL 1141 and *Staphylococcus aureus* mscL 334; **b)** activity of modified/unwashed knitted fabric samples against *Bacillus subtilis* mscL 1141 and *Staphylococcus aureus* mscL 334.

The samples of unmodified knitted fabric did not show antibacterial activity against both cultures, and the sample with *subtilis* bacteria was observed under and around the sample (Fig. 4.10 a)).

The antibacterial effect of the modified knitted cloth is ensured not only in contact with the sample, but also by forming an inhibition zone, a special activity is observed against the bacterium *Staphylococcus aureus* (Fig. 4.10 b)).

After HT treatment, no zone of inhibition was observed against the *Bacillus subtilis* mscL 1141 bacteria, but the growth around and under the sample was not detected; given that hosiery products fit tightly against the wearer's skin, the habitat of *Bacillus subtilis* will be compromised. In contrast, antibacterial activity against *Staphylococcus aureus* mscL 334 also showed a zone of inhibition.

Comparative Analysis of Air Permeability of Knitted Fabrics (Cotton/Polyester/Elastane)

After modification and HT post-treatment, a slight decrease in AP in the range of 2.4–6.3 % can be observed in the group of all samples. This means that by modifying only a part of the

threads of the knitted fabric, the decrease in AP practically does not affect the wearing comfort. After HT treatment, the AP reduction of the knitted cloths with modified cotton yarn in variants ranging from 2–6 % (Table 4.5) is relatively small and can practically be considered as having no effect on wearing comfort.

In comparison, the AP of the fabric knitted from unmodified cotton/PES/elastane yarns is 25 % lower than the AP averages of unmodified cotton/PA/elastane fabric (Table 4.7), which could be explained by the different linearity of cotton PA/elastane and PES/elastane density as well as thread percentages.

Table 4.6

AP and VP Results of Knitted Fabrics (75 % CO / 21 % PES / 4 % Elastane).

	Control	M/W/1:8/5	M/W/1:12/5	M/W/1:8/15	M/W/1:12/15
Air permeability, mm/s	386.5	362.3	368.9	377.1	365.6
+/-, mm/s	14.1	24.7	20.5	20.7	17.7
Decrease, %		-6.3 %	-4.5 %	-2.4 %	-5.4 %
Relative vapour permeability, %	50.9*	48.6	50.7	53.4	51.7
Decrease/increase, %		4.5 %	0.4 %	-4.9 %	-1.6 %

* The vapour permeability index is determined in the centre of the plan (1:10/10) with a modified yarn in the composition.

In contrast, in modified cotton yarn/PES variants, AP has decreased by only 8–12 % compared to the PA/elastane-containing cloth variants in the range of 17–24 % (Table 4.9).

The relative water VP of the modified cotton/PES/elastane variant within the range of 48.6–53.4 % includes the average indicator of the modified cotton/PA/elastane variant of 49.1 %, which practically does not differ from the variant with unmodified cotton yarn in the composition (49.4 %).

Summary and Conclusions of Chapter 4

1. The patent-protected solution proposed in the Doctoral Thesis envisages dividing the production of platinized plain weave modified knitwear into two consecutive processes:
 - modification of cotton yarn to give it functional properties;
 - preparation of the modified yarn for knitting and designing of the knitting process by integrating the modified yarn with unmodified polyamide/elastane or polyester/elastane threads in a platinized knitted structure, providing, if necessary, including the subroutines for weaving sensors and electroconductive threads into the control program of the knitting machine.
2. The process of obtaining a modified cotton yarn is divided into ten steps, providing for the cleaning of the industrially obtained yarn from the impurities introduced during the technological processes, aging in a climate chamber, synthesis of the sol solution and modification of the yarn, as well as concluding the consolidation of the coating with the final hydrothermal treatment. When preparing for knitting, the modified yarn is coated during the rewinding process to increase flexibility; the modified yarn is combined with polyamide/elastane threads or polyester/elastane threads during the knitting process.
3. SEM micrographs and EDX analysis show that the topography of the fibre surface and the relative percentage distribution of chemical elements change during the steps of the modification process, agglomerates have formed in the coating of the surface of the modified yarn, fibres have stuck together in the places of periodic dressings, which makes it difficult to access the modifying sol. In the process of the final hydrothermal treatment, the coating consolidates with the surface of the fibres and the relative percentage distribution of elements on the surface of the fibres stabilizes. In the industrial process, a better control of the through-flow of the sol is possible, ensuring an even access of the modifying composition and stabilizing the other process parameters and thus the volumes and properties of the applied coating.
4. The breaking strength of the modified yarn increases on average by 17 %, the linear density by 16 %; if the parameters of the sol synthesis are strictly observed, the elongation at break decreases slightly.
5. In the samples of knitted fabrics with the modified cotton yarn, the stitch density increases by 2.6 %; as porosity decreases, air permeability decreases by an average of 21 %; the decrease in vapour permeability does not exceed 5 %, with much less impact on the characteristics of the wearing comfort compared to woven cloths. Optimum soaking time and sol solution/yarn mass ratio allow to minimize air permeability reduction of knitted fabric with a modified cotton yarn component.
6. The antibacterial tests with the disk diffusion method against the gram-positive bacteria *Staphylococcus aureus* mscL 334 and *Bacillus subtilis* mscL 1141 show that the test samples have antibacterial activity against the tested bacteria, as there is no growth on,

under, and around the samples; inhibition free from the test bacteria has formed an area that improves the wearer's comfort by preventing the growth of bacteria, while the impact of using the product on the environment decreases, as the time between washes increases, the consumption of detergents and electricity decreases, and the longevity of the sock product increases.

7. The wear resistance of knitted fabrics with a modified cotton yarn content increases significantly. Serious surface defects were detected after 15.000 friction cycles and in control variants after 5.000 cycles, which is a significant improvement in the performance of knitted fabrics, considering the low wear resistance of cotton knits.
8. The additions made to the spectrum acquisition and spectral analysis methodology, adapting it to the study of platinized knit structures, allow tracking both the effects of yarn modification and the influence of the parameters of the technological process of platinized plain knitting and developing the corrections to achieve certain characteristics of the final product.

PROPOSALS AND RECOMMENDATIONS

1. The modification of industrially produced cotton/polyamide platinized knitted socks by applying the adapted sol-gel process is useful for ensuring anti-microbial protection, mechanical properties, including increasing wear resistance, and obtaining an “easy cleaning” effect because of the hydrophobization of the fibre surface.
2. When trying to replace hydrofluoric acid with the more environmentally friendly acetic acid in the composition of the adapted sol-gel technology, the expected functional properties were realized only with a very limited set of technological parameters in a weaker form, or the antibacterial effect was not realized at all. In addition, the observations show that hydrofluoric acid in the sol performs not only the functions of a catalyst, but as shown by EDS and spectral analysis, during the sol-gel process, C-Fn functional chemical groups important for providing modifying effects on textiles are formed in the coating composition.
3. Despite the decrease in the porosity of the internal fibres/threads when the modifying coating isolates the internal pores, due to the structure of the platinized knitted fabric, the properties determining the wearing comfort decrease relatively little (air permeability) or practically not at all/even slightly increase (vapour permeability), due to the interaction of the hydrophilic surface of the textile and the created hydrophobic layer excess moisture is efficiently removed from the “wearer's skin-textile” contact zone.
4. It is possible to combine the sol-gel process adapted to the modification of knitted fabric of mixed fibre composition with the final hydrothermal treatment process of traditionally used sock products, including a section for impregnating/spraying socks with a sol solution.



Fig. 4.11. Finishing hydrothermal treatment of socks [36].

5. Considering the rapid introduction of various wearable electronics into the market, technologies for modifying cotton yarn before knitting were developed as part of the

Thesis with the aim not to expose the electronic components embedded in the knitting process to the sol-gel process and preserve their functional performance in socks.

6. A comparative analysis of modified cotton yarn/PA and modified cotton yarn/PES platinized knitwear allows us to conclude that the planned functional and comfort characteristics are provided in both cases, they vary in a narrow interval depending on the composition of the sol and the process parameters, and the intensity of the effect is more influenced by the interaction of parameters than each parameter individually.
7. Comparing the comfort characteristics of the knit options containing PA and PES threads, it was concluded that the reduction in air permeability of the modified cotton/PES knitted structures does not exceed 10 % and the relative vapour permeability in some variants even increases, while at the same time the average decrease in air permeability of the knitted structures with PA threads reaches 20 %, the decrease in relative vapour permeability is negligible.
8. The regression equations obtained in the research process and the corresponding sections of the echo surfaces can be used in the process of selecting and harmonizing the composition of the bench and the technological parameters of the process according to the intended use.
9. The method of additional processing of data obtained by Fourier transform infrared spectroscopy developed in the work allows to obtain not only qualitative, but also quantitative data for the control of technological process parameters and evaluation of modification effects of mixed fibre composition platinized plain knitted fabrics.
10. Incorporation of modified cotton yarn components in the knitting process in the range of 70–80 % (keeping the synthetic yarn composition to 30 %) into the platinized plain weave structure ensures the antimicrobial activity of the mixed fibre platinized plain weave knit, not only by preventing the growth of micro-organisms in the skin-textile zone, but also by providing a relatively wide zone of inhibition around the modified cotton yarns, thereby protecting the knitted structure and the wearable electronic components incorporated therein as a whole. At the same time, the comfort properties of the wearer are maintained.
11. The introduction of a particular yarn modification into production would be practical in a yarn-spinning mill, which traditionally has facilities for re-shedding yarns onto crosses, and often onto filaments if dyeing of the yarns is envisaged. This would be the optimal case, as the appropriate dyeing equipment can be applied to impregnate the yarn with a sol solution if necessary, completing the process on the drying line of the plant, which would be the most economically viable option.

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