

BIODEGRADABLE NONWOVEN ACTIVATED POLYESTER WITH CHITOSAN: POTENTIAL APPLICATION IN THE COSMETIC INDUSTRY

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Abstract

Textile products enriched with natural substances, e.g. hyaluronic acid, plant hydrolates, collagen and chitosan, may find wide application in cosmetics because of increasing consumer interest in natural products. Furthermore, in view of global environmental pollution, products that are produced through biochemical changes as a result of composting are sought. This makes it possible to enter such designed cosmetic products into the scheme of the currently desired circular economy. Compostable textiles are an ecological alternative to product backlogs and polluting the environment in the form of post-consumer waste. Therefore, this research work developed a technology for applying natural substances on a biodegradable polyester fibrous substrate. This study developed the optimal composition of a mixture consisting of natural substances with properties applicable to the cosmetic industry, for applications such as cosmetic masks to improve the appearance of the skin. The composition of active substances that have beneficial effects on the skin, e.g. moisturizing, regenerating, antibacterial and caring, was determined. The mixture was effectively applied on a spunbound nonwoven substrate made from aliphatic-aromatic copolyester by impregnation. The employed polymer degraded in a compost environment and its modifiers additionally supported this process. The unique composition of the applied coating layer consisted of a mixture of sodium hyaluronate, collagen, bitter orange blossom hydrolate (Neroli) and chitosan lactate. The coated nonwoven fabric was subjected to physical, mechanical, microbiological as well as chemical purity and structural tests (Fourier transform infrared spectroscopy and scanning electron microscopy) and degree of degradation in a compost environment was assessed on the basis of its weight loss.

Keywords: *polyester nonwoven, cosmetic mask, chitosan, hyaluronic acid, collagen, Neroli hydrolate*

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1. Introduction

Due to high environmental pollution from waste of common synthetic polymers, there has been a trend towards replacing them with either natural or synthetic polymers that are subject to environmental degradation. On a global scale, this problem particularly affects the poorest countries, where waste is often stored improperly. Therefore, the European Union (EU) has intensively promoted a circular economy, which allows for rational but above all ecological management of raw materials and waste. This policy focuses on a life cycle of the product, from raw material through product to waste. Technological elements are also included in the product life cycle, such as consumption of water, chemicals and energy as well as emissions of carbon dioxide (CO_2) and other gases [1]. Many research centres have performed numerous studies on the use of polymers of a natural origin, including chitin and its derivatives, e.g. chitosan and butyryl-acetyl chitin

[2–5] These polymers are primarily used in medicine [6–9]. The reason for this use is the unique biological properties of chitosan, including bacteriostatic, bioactivity, anti-cancer and haemostatic properties, as well as biocompatibility. Therefore, it is used for construction of multifunctional dressing materials, implants (e.g. partially resorbable surgical meshes for hernia treatment, blood vessel prostheses and implants used in peripheral nerve regeneration) and in tissue engineering for bone and cartilage tissue reconstruction [10–12]. Research on the use of this polymer in the pharmaceutical industry has been conducted since 1980 [13, 14]. Chitosan is used as a carrier in the controlled drug release process (e.g. of naproxen) because it shows mucoadhesive, gelling, transfection and penetration-enhancing properties [15].

Research that has been conducted for many years on the possible use of chitosan in the cosmetic and hygiene industry has indicated that the cosmetic market is looking for a new range of products that can be constantly improved and modified [16–19]. Chitosan is used in the cosmetic industry due to its physicochemical and biological properties. In cosmetics, the cationic nature of this polymer is important (chitosan and hair carry opposite electrical charges), as well as its bacteriostatic, fungistatic, antistatic, film forming and moisture-retaining properties; therefore, it is used in hair care cosmetics. Chitosan is also a very interesting component in cosmetic preparations due to its compatibility with other ingredients such as starch, glucose, sucrose, polyols, oils, fats, waxes, acids, nonionic emulsifiers and nonionic water-soluble gums. Chitosan and its derivatives can be combined with other moisturizers, sunscreens and bioactive products used in cosmetic preparations and facilitate their action, e.g. some chitosan derivatives may have an emulsifying effect [17, 20–22]. In Asian countries, there are cosmetic masks made of viscose or Tencel nonwoven fabric with the addition of chitosan or masks made from chitosan

fibres, while in Europe products in liquid form are available. There are commercial products based on chitosan currently available on the market for cosmetic use, e.g. HydamerTM, ZenvivoTM, Ritachitosan® and Chitosan MM222, among many other [17].

The cosmetic industry is rapidly growing throughout the world. It is estimated according to The Reimagining Growth in the Global Beauty Industry, that the global cosmetic market is worth USD 445 trillion and its value is constantly increasing. The value of the Polish cosmetic market in 2016 amounted to PLN 16 billion. It is estimated that in 2021 the value of the Polish cosmetic industry will reach PLN 20 billion. One of the main reasons for such large increases will be exports to the EU market, as well as outside Europe, including Asian countries. Such opportunities lead to the search for new ecological products that will meet the growing expectations of customers. Consumers are

increasingly paying attention to natural cosmetics, which are safe for the user and also for the environment. In Western Europe, when choosing a product, more and more consumers consider elements of social responsibility, even if they are not the main determinants of choosing a particular brand. Throughout the world, already over 30% of consumers expect cosmetics to be based on natural ingredients (especially skin cosmetics) [23]. The cosmetic market is very diverse in terms of products offered. Face masks with, for example, moisturizing, smoothing and anti-ageing properties are the current trend; they came to Europe from Asia (mainly Korea), where this type of product is widely used. It is now becoming more and more popular in Europe. According to the Transparency Market Research Institute experts, the value of the face mask market is growing. In 2015, the value of this segment was estimated globally at USD 160.4 million, but analysts expect that by 2024 it will reach USD 336.7 million. Unfortunately, many of these products contain chemical preservatives, substances that improve product properties, and fillers i.e. polyethylene glycol (PEG), polypropylene glycol (PPG), parabens, sodium laureth sulfate (SLS/SLES), phthalates, silicones and alcohols. Using them for a long time on the skin can cause very unpleasant symptoms – i.e. allergy, irritation, a drying effect, redness, rashes and inflammation of the skin – and in the worst case it may be carcinogenic (as in the case of PEG or PPG). Therefore, cosmetics based on natural products are currently appearing on the market, because consumers expect a change in this direction. The natural cosmetic market is still a niche, but due to a change in the mentality of consumers it will become increasingly popular over the next few years.

Commercially available nonwoven cosmetic products are mainly based on natural polymers that are biodegradable in the natural environment or nonbiodegradable polymers of petrochemical origin. In the group of natural polymers, two types of raw material, cellulose and cotton, are commonly used for the production of wipes, hygiene products (liners, tampons), face masks, cosmetic pads, etc. From the group of petrochemical raw materials for cosmetics, polypropylene, polyesters and polyamide are used, which are not biodegradable in the natural environment [24]. Many cosmetic products, including wet wipes, baby wipes and face masks, contain a mixed material of polyester (PET) fibres in combination with cellulose as a woven fabric [25]. Textile nonbiodegradable polymer products are post-consumer waste that is disposed of in landfills. However, there are no biodegradable petrochemical nonwoven cosmetic products.

Therefore, as part of research work, a material from a biodegradable aliphatic-aromatic copolyester with an active layer based on natural substances was developed. Synthesis technology was developed for polymer designed for processing into nonwoven products using the spunbond method, and the composition of cosmetic substances and the method of applying them to the nonwoven products were selected for use in cosmetic masks, moisturizing wipes and other applications. The active cosmetic substance layer consisted of a mixture of sodium hyaluronates, bitter orange blossom hydrolate (Neroli), collagen and chitosan lactate. Collagen, hyaluronic acid and Neroli hydrolate have care properties and are widely used in cosmetics, and when applied to a nonwoven fabric, they can perfectly fulfil a cosmetic function, e.g. in the form of an ‘active’ mask. Chitosan lactate additionally supports the antibacterial effect but also improves mechanical and absorption properties and lowers the pH to the value typical for skin. Sodium hyaluronate is often used in the cosmetic industry due to its moisturizing, protective and anti-ageing properties. It is used, among other components, in cosmetic products (creams, masks, tonics, conditioners, etc.) for skin care in face, neck and eye area as well as in body care products against cellulite and stretch marks [26, 27].

2. Materials and Methods

2.1. Synthesis of Polymer

The synthesis of the aliphatic–aromatic copolyester was carried out in a 30 L Fourne reactor (Germany) in two steps: (1) an ester exchange and (2) a polycondensation process. During the ester exchange, there was transesterification of terephthalic acid dimethyl ester and a mixture of aliphatic dicarboxylic acid dimethyl esters with 1,4-butandiol. The transesterification process was carried out at atmospheric pressure, at temperature 165–225°C in the presence of tetrabutyl orthotitanate (TBOT) as a catalyst. In the pre-polycondensation process, excess of 1,4-butandiol was distilled off. The pre-polycondensation process was carried out at a pressure ranging from atmospheric to about 2 mmHg. The reaction was then carried out at a temperature of about 240–250°C in the presence of the TBOT and under a vacuum of 0.4 mmHg. The nucleating agent was a suspension of sodium carbonate in 1,4-butandiol. As a result of the synthesis, an aliphatic–aromatic copolyester with the ratio of aliphatic/aromatic component (Al/Ar 60/40) was obtained [28].

Materials used in the synthesis:

- Terephthalic acid dimethyl ester (DMT), purity 99.8% (Mogilewo, Belarus);
- 1,4 butanediol (1,4 BD, purity 99.5%, PPH Standard);
- Uniestrol (experimental Plant ‘Organika’ Sp. z o.o. Poland), molar composition: dimethyl succinate 15–25%; dimethyl glutarate 25%–50%; dimethyl adipate 25%–45%;
- TBOT (Sigma-Aldrich);
- Sodium carbonate (purity 99.8%, Chempur, Poland).

None of the utilized materials appear in the list of banned substances in cosmetic products: Regulation of the European Parliament (EC) No. 1223/2009 on cosmetic products.

2.2. Spinning of the Nonwoven Fabric by the Spunbonding Method

The process of forming nonwoven fabric using the spunbonding method was carried out in a laboratory setup. During spinning, the polymer was stored in a HR50 pellet dryer (Piovan, Poland) at 60°C, with a dew point of 36.9°C. In the spinning process, a 210-hole spinneret was used, and the capillary diameter was 0.3 and 0.9 mm, respectively. Spinning was carried out at 185°C, and the process yield was 0.48 g/min/hole. This product generated a nonwoven substrate with a surface density of 77 g/m².

2.3. Active Layer

Polyester nonwoven fabric was impregnated with natural substances constituting the composition of the active layer. The selected compounds were characterized by their care and moisturizing properties. Preparation of usable form, employed chitosan lactate (ChitoClear 43010 HQG 110 TM4848, Primex ehf., Iceland). It was characterized by the following physicochemical parameters: molar mass (M_v) 317.7 kDa, degree of deacetylation (DD) 85.8% and ash content 0.18 wt%. Substances constituting the active layer were (Table 1):

Sodium hyaluronate, with a molar mass of 1,320 kDa (high hyaluronic acid [HHA], purchased from MakingCosmetics, USA);

Sodium hyaluronate (small hyaluronic acid (SLMW) with a molar mass of 10 kDa (small hyaluronic acid [SHA], MakingCosmetics);

Soluble collagen, variant 2 (Proteina, Poland);

Bitter orange blossom (Neroli) hydrolate (Biochemia Urody, Poland);

Chitosan lactate (pH 5.5, a polymer content of 2.0%, M_v of 310.0 kDa and DD of 85.8%); and

Pure lactic acid (88%, Avantor, Poland).

Table 1. Properties of selected substances used in the active layer.

Substance	Cosmetic properties
Hyaluronic acid [29, 30]	Moistening, protection, anti-ageing, conditioning, anti-cellulite, anti-stretchmarks
Collagen [31]	Anti-ageing, nontoxic, improving skin tension and elasticity, moistening
Bitter orange blossom (Neroli) hydrolate [32]	Sedative, antidepressant, treats insomnia, relaxant for smooth muscles, suitable for all skin types, nonirritant, non-sensitizing
Chitosan [17, 20–22]	Bacteriostatic, fungistatic, antistatic, film-forming, moisture retaining

In the first stage, the nonwoven material was impregnated with a 3% aqueous collagen dispersion in dilute citric acid for 2 min. The sample was then dried at room temperature. In the second stage, the sample was impregnated in an aqueous solution containing 0.9% SHA, 0.1% HHA, Neroli hydrolate and a 2% solution of chitosan in lactic acid for 5 min. The sample was dried at room temperature on a Teflon plate. Collagen was applied separately it could be easily degraded in the solutions used.

2.4. Physicochemical Analysis of Copolyester

Estimation of copolyester melt flow index (MFI): polymer at 190°C was extruded through a spinneret with a 2.0 mm capillary at a piston load of 2.16 kg. The extrusion proceeded in a defined time, and MFI was calculated.

Relative viscosity (η_{rel}) of copolyester was measured in a chloroform solution at 25°C with a polymer concentration of 0.2 g/100 cm³. An Ubbelohde-type viscometer with a 0 A and k = 0.00498 capillary was used.

The thermal characteristic of the copolyester samples was studied by differential scanning calorimetry (DSC) with the use of a Diamond apparatus (Perkin Elmer, USA) equipped with an Intracooler II, an AD-2Z microscale and Pyris software.

Material structure was examined by scanning electron microscopy (SEM) using a Quanta 200 microscope (FEI Co, USA). Samples sputtered with a 20 nm gold layer were tested in a high vacuum at an electron beam accelerating voltage of 5 kV.

2.5. Physical–Mechanical Examination

Tests were made at standard environmental conditions (20 ± 2°C and relative humidity [RH] 65 ± 4%) according to standard PN-EN ISO 139:2006 [33]. The following parameters were estimated:

Surface density according to standard PN-EN 29073-1:1994 [34];

Tensile force and elongation of conditioned samples were measured according to standard PN-EN 29073-3:1994. The measurements were made on the tenacity tester model 5544 (Instron, United Kingdom) [35];

Bending length along and across the sample were measured according to standard PN-EN ISO 9073-7:2011. The measurements were made on the apparatus for measuring flexural rigidity for samples cut along and across the nonwoven substrate [36];

Liquid absorption capacity (LAC) and capillary increase of the fluid were measured according to standard PN-EN ISO 9073-6; distilled water at room temperature was used as test liquid [37].

2.6. Microbiological Activity

Evaluation of the antibacterial effect of the produced nonwovens was carried out in accordance with PN-EN ISO 20743:2013. *Staphylococcus aureus* (strain ATCC 6538) from the American Collection of Pure Cultures was used in the test, which comprised inoculating nonwoven samples with a bacterial suspension of a specified density of cells and determining the number of colony forming units (cfu) before and after 0.5 and 2-h incubation [38].

2.7. Chemical Purity

Simulating delivery in standard application, the dynamic extraction method was employed according to PN-EN ISO 10993-12:2009 and to the demands of USP 38 NF 33 [39, 40]. Water for injection was used as the extractant (pH 5.96). The process was run in a shaker (shaking parameters 150 rpm) with a SW 23 shaking water bath (Julabo, Germany) at $37 \pm 1^\circ\text{C}$ for 30 ± 2 min. The time of the test simulated potential use of the product as a cosmetic mask. Commercially available cosmetic products in the same form as the tested product are usually used for 15–20 min. The assay used the normalized surface area of 6 cm^2 per 1 cm^3 of the extractant. The following parameters of chemical purity were estimated in three parallel tests: pH, turbidity, content of water-soluble substance and content of heavy metals.

The pH was measured with a pH meter and Blue Line 14 pH electrodes (Schott Instruments, Germany) at ambient temperature according to standard PN-EN ISO 3071:2007 [41].

Turbidity was estimated with a turbidimetric method according to European Pharmacopoeia 8.0 by measuring scattered light with a UV/VIS spectrophotometer (model 5625, Unicam, United Kingdom). A suspension of formazine was used as basic reference standard equal to 4000 NTU; it is a blend of hydrazine sulfate and hexamethylenetetramine (urotropine) [42].

The content of water-soluble substances was determined according to PN-P-0478/06:1988 and PN-EN ISO 10993-12:2009 [39, 43]. The amount of dry residue in the water extract is estimated with this method. The residue is the sum of water-soluble and water-insoluble matter (turbid extracts) after the amount of evaporated water is determined according to the standard.

The content of heavy metal ions was determined by atomic absorption spectrometry (ContraAA 700, Analytik Jena, Germany). Cadmium (Cd), chromium (Cr), lead (Pb) and zinc (Zn) were directly determined in aqueous extracts by the flame method; arsenic (As) was determined by electrothermal atomization; and mercury (Hg) was determined by cold vapour generation.

2.8. Fourier Transform Infrared Spectroscopy (FTIR)

The test sample were analysed by attenuated total reflectance (ATR) to observe changes in the nonwoven structure after modification with collagen, hyaluronic acid, Neroli hydrolate and chitosan salts. The analysis was performed on a FTIR Nicolet iS50 spectrophotometer (Thermo Scientific, United States).

2.9. Biodegradation

Biodegradability was tested in a compost medium by measuring the weight loss according to standards PN-EN 14045:2005, PN-EN 14806:2010 and PN-EN ISO 20200:2016-01 [44–46]. The tested samples were placed in a compost medium containing aerobic microorganisms. Reactors with the tested samples were placed in a thermal chamber in which constant conditions were maintained (temperature $58 \pm 2^\circ\text{C}$, RH 40–70%).

3. Results and Discussion

The main goal of the research was to develop a technology for producing a biodegradable matrix from an aliphatic-aromatic copolyester, activated by a unique composition of natural substances. The manufactured product would be environmentally friendly and would meet the requirements of a circular economy, a system which is currently intensively supported by the EU Parliament. The assumption of the study was to produce a cosmetic product showing care and moisturizing effects and that will not constitute environmental ballast in the form of post-use waste.

The copolyester used in the tests was characterized by good thermal parameters: the melt crystallization temperature (T_c) was $> 40^\circ\text{C}$, and the melting point (T_m) was 113°C . The melt flow index (MFI) was 30–43 g/10 min. The higher the melt flow rate, the easier it would be for a given polymer to be processed into a nonwoven substrate by the spunbonding method. The relative viscosity of the polymer was 1.14. The polymer had good processing properties. The nonwoven substrate produced by spunbonding had a surface density of 77 g/m^2 .

In the next stage of the study, the nonwoven substrate was coated with a mixture of natural substances – sodium hyaluronates, Neroli hydrolate, collagen and chitosan lactate – and its mechanical, microbiological and physicochemical properties were evaluated. The nonwoven substrate's susceptibility to degradation in the compost environment was also determined based on weight loss. All tests were carried out in accredited laboratories in accordance with the standard PN-EN ISO/IEC 17025.

3.1. Physico-mechanical Properties of the Base Nonwoven Fabric With and Without an Active Layer

The assessment of the mechanical properties of the base nonwoven fabric with and without an active layer was carried out in an accredited metrological laboratory (certificate number AB 338). The base nonwoven fabric had a surface density of 77 g/m^2 , which after activation with natural components increased to 103 g/m^2 ; for the variant with active substances and chitosan, the surface density was 96 g/m^2 . The nonwoven fabric with a surface density of 77 g/m^2 was used because during the development of optimal thermal forming conditions for spunbonding, the applied conditions produced a homogeneous fibrous base at this surface density. All variants of the nonwoven fabric were tested using the Instron model 5544 machine, and the results are presented in Figs. 1–3.

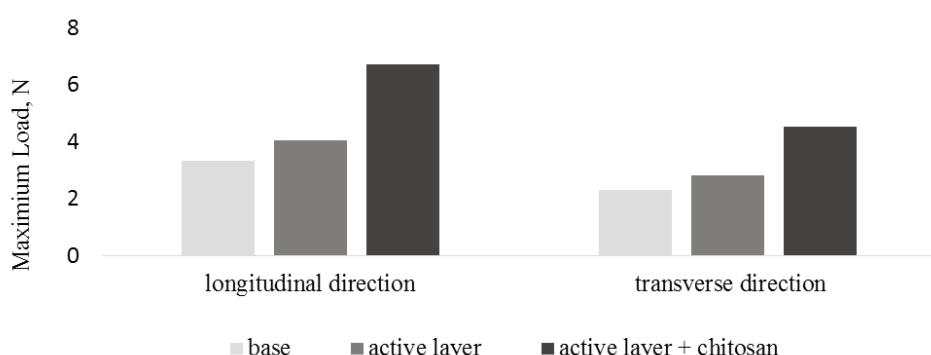


Figure 1. Maximum load for the base nonwoven fabric with and without an active layer.

As a result of the application of the active layer on the base nonwoven fabric, there was an increase in mechanical parameters. For the active layer with the addition of chitosan lactate, breaking force increased 100% in the longitudinal direction and 94% in the transverse direction relative to the base nonwoven fabric (Fig. 1). The strength of the nonwoven also increased after surface modification by 100% for the longitudinal direction and 99% for the transverse direction after applying the active layer with chitosan lactate (Fig. 2).

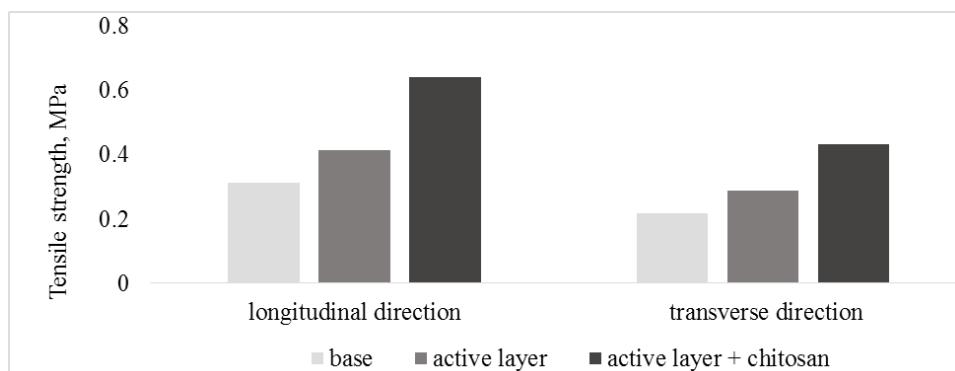


Figure 2. Tensile strength for the base nonwoven fabric with and without an active layer.

With the addition of the active layer, the elongation decreased 90% in the longitudinal direction and 101% in the transverse direction compared with the base nonwoven fabric (Fig. 3). The fabric with an active layer enriched with chitosan lactate exhibited a further decrease in elongation in both directions, as a result of a stiffening effect caused by the applied substances. The obtained base nonwoven fabric had a very low bending length (Fig. 4) and general bending rigidity (Fig. 5), which translates into very good product drapability. The bending length and general bending rigidity of the nonwoven fabric increased after modification, a phenomenon associated with a slight decrease in drapability, but the maximum bending length of about 2.5 cm indicates good performance of the obtained products (Fig. 4).

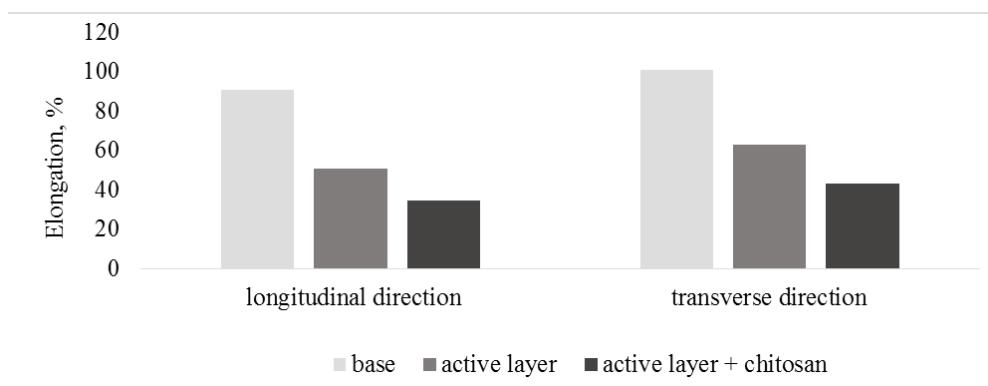


Figure 3. Elongation for the base nonwoven fabric with and without an active layer.

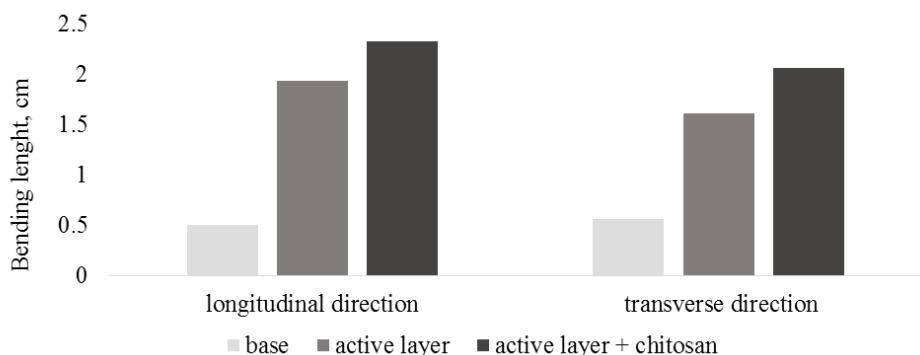


Figure 4. Bending length for the base nonwoven and the base fabric with and without an active layer.

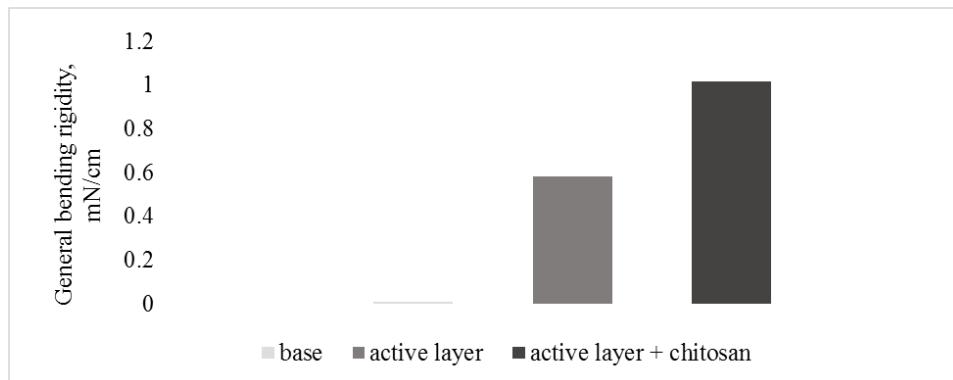


Figure 5. General bending rigidity for the base nonwoven fabric with and without an active layer.

The base nonwoven fabric was characterized by very low liquid absorption capacity. The applied active layers improved this factor, which is important in the case of cosmetic or hygienic use. The addition of chitosan lactate did not significantly affect this parameter (Fig. 6).

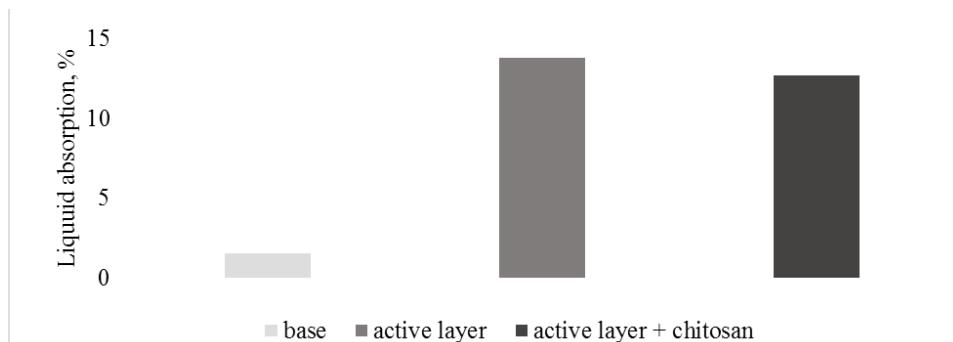


Figure 6. Liquid absorption for the base nonwoven fabric with and without an active layer.

3.2. Microbiological Properties of the Base Nonwoven Fabric With and Without an Active Layer

The assessment of the microbiological properties of the base nonwoven fabric with and without an active layer was carried out at an accredited microbiological laboratory (certificate number AB 338). The microbiological tests were performed according to the standard PN-EN ISO 20743:2013 against *S. aureus*, a bacterium responsible for frequent skin infections. The tests were conducted to simulate potential use of the product as a cosmetic/hygiene product (Fig. 7). For the base nonwoven fabric, the number of microorganisms increased as a function of time. However, the nonwoven fabric with the active layer enriched with chitosan lactate presented a lower level of microorganisms (3.0×10^1 cfu/mL) after a 2-h incubation. For the nonwoven with the addition of active substances (without chitosan), there were fewer microorganisms compared with the base nonwoven fabric. After a 30-min incubation, there was an increase in the number of microorganisms, and only after 2 h did the number of microorganisms decrease (to 4.2×10^4 cfu/mL). The inhibitory effect on microorganism growth was associated with chitosan lactate.

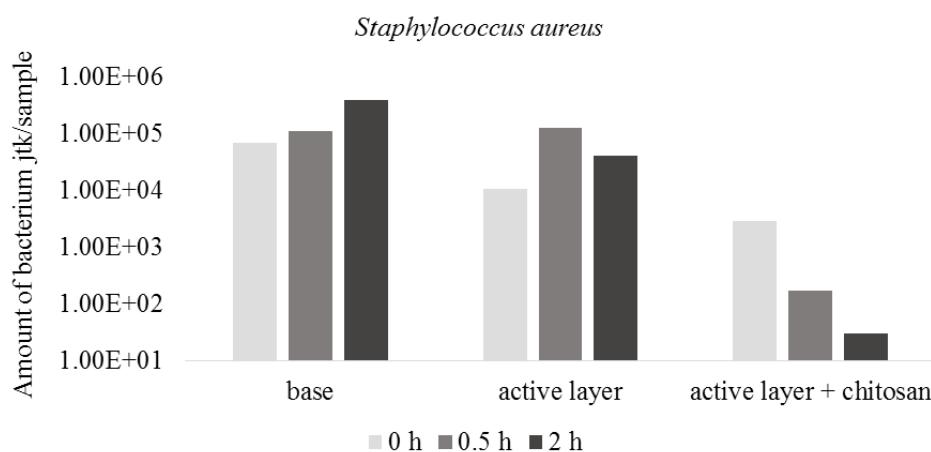


Figure 7. The change in the amount of *Staphylococcus aureus* on the base nonwoven fabric with and without an active layer at different incubation times.

3.3. Physicochemical Properties of the Base Nonwoven Fabric With and Without an Active Layer

The base nonwoven fabric with and without the active layer with chitosan lactate was subjected to dynamic extraction in an aqueous environment at $37 \pm 1^\circ\text{C}$ for 30 min. The extraction simulated the potential use of the material as a cosmetic/hygiene product. The aqueous extract was subjected to physicochemical analysis. The pH of the extract (Fig. 8) from the base nonwoven fabric was 5.7, while the pH of the extract from nonwoven fabric activated with natural substances was 5.1. The addition of chitosan lactate to the active layer reduced the pH to 4.7, which is a very beneficial phenomenon in the case of cosmetic application, because higher pH values favour bacterial infections. As the skin's natural pH is in the range of pH 3.5–5.5, the obtained test results prove that the selected natural substances utilized for the active layer improve the quality and safety of the product in case of cosmetic application.

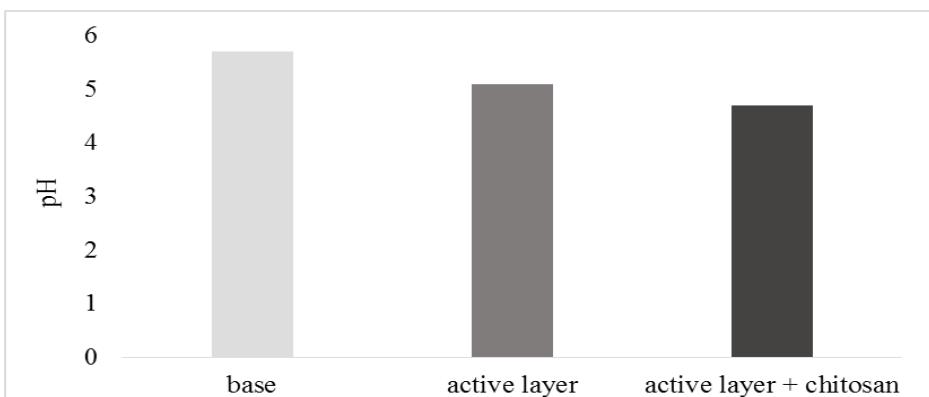


Figure 8. pH of aqueous extracts from the base fabric with and without an active layer.

The content of soluble substances in the extracts was also determined (Fig. 9) For the base nonwoven fabric, soluble substances accounted for 0.007 wt%, whereas for activated nonwoven fabric there was an increase to 4.830 wt%, and after the addition of chitosan lactate, the level further increased to 5.330 wt%. The substances applied to the nonwoven fabric can freely migrate to the extract, which is beneficial in case of potential use of the product in cosmetic applications.

Tests were also carried out for harmful substances, i.e. heavy metals, using the AAS method, for extracts from the base nonwoven fabric with and without an active layer with chitosan lactate (Table 2). The determined heavy metal content was below the level of detection.

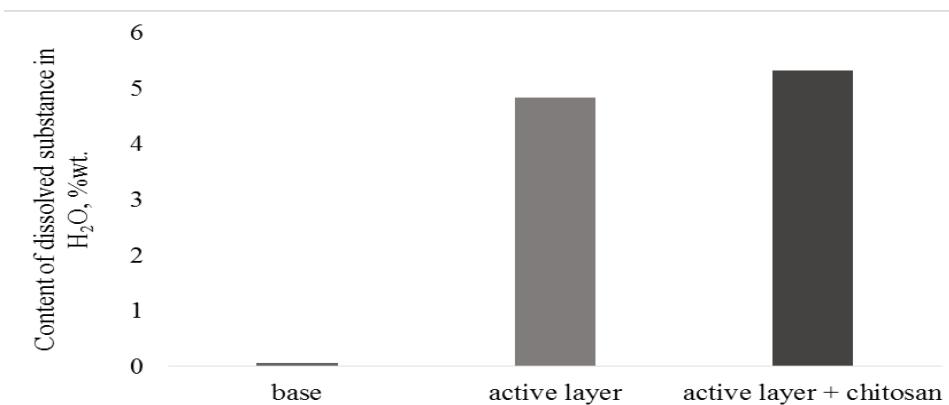


Figure 9. Content of dissolved substances in aqueous extracts from the base nonwoven fabric with and without an active layer.

Table 2. Heavy metal content in extracts from the base fabric with and without an active layer enriched with chitosan lactate.

Element	Unit	Base	Base with an active layer
Al	mg/dm ³ of the aqueous extract	< 0.5	< 0.5
Cd		< 0.02	< 0.02
Cr		< 0.2	< 0.2
Pb		< 0.15	< 0.15
Zn		< 0.015	< 0.015
Hg		< 0.0001	< 0.0001

3.4. FTIR of the Base Nonwoven Fabric With and Without an Active Layer

The nonwoven fabrics were next subjected to FTIR using the ATR technique; the spectra are presented in Fig. 10. After activation with natural substances with chitosan lactate, there were several characteristic peaks: amide I (1591 cm^{-1}) and hydroxyl groups at 3366 cm^{-1} . These data indicate that chitosan lactate had been effectively applied to the biodegradable base nonwoven fabric.

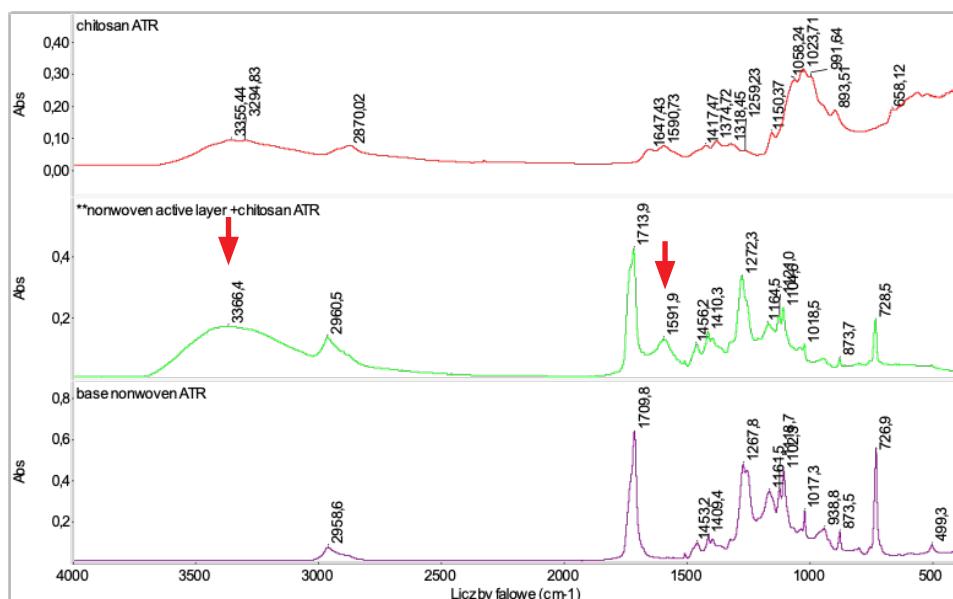


Figure 10. Fourier transform infrared–attenuated total reflectance spectra for the base nonwoven fabric with and without an active layer enriched with chitosan lactate.

3.5. Surface Topography Analysis of the Base Nonwoven Fabric With and Without an Active Layer using SEM

The surface appearance of the obtained nonwoven materials was evaluated using SEM. In the sample of polyester nonwoven fabric with an active layer enriched with chitosan (Fig. 11), there was an uneven surface coverage with the active layer. In

addition, most of the cosmetic substances were effectively applied onto the fibres of the base nonwoven fabric.

3.6. Biodegradation of a Base Nonwoven Fabric With and Without an Active Layer

Tests were carried out in an accredited biodegradation laboratory to determine the degree of biodegradation of the nonwoven fabrics in the presence of aerobic microorganisms based on the weight loss method. The tests were carried out in a compost environment at $58 \pm 2^\circ\text{C}$ and an RH of 40–70%. The results are shown in Fig. 12. The base nonwoven fabric incubated for 28 days presented a weight loss of 24.6 wt%. For the activated nonwoven fabric, the weight loss was 17.8 wt% after 7 days and 36.5 wt% after 28 days. The addition of chitosan to the active layer did not change the dynamics of the biodegradation process in compost environment over time.

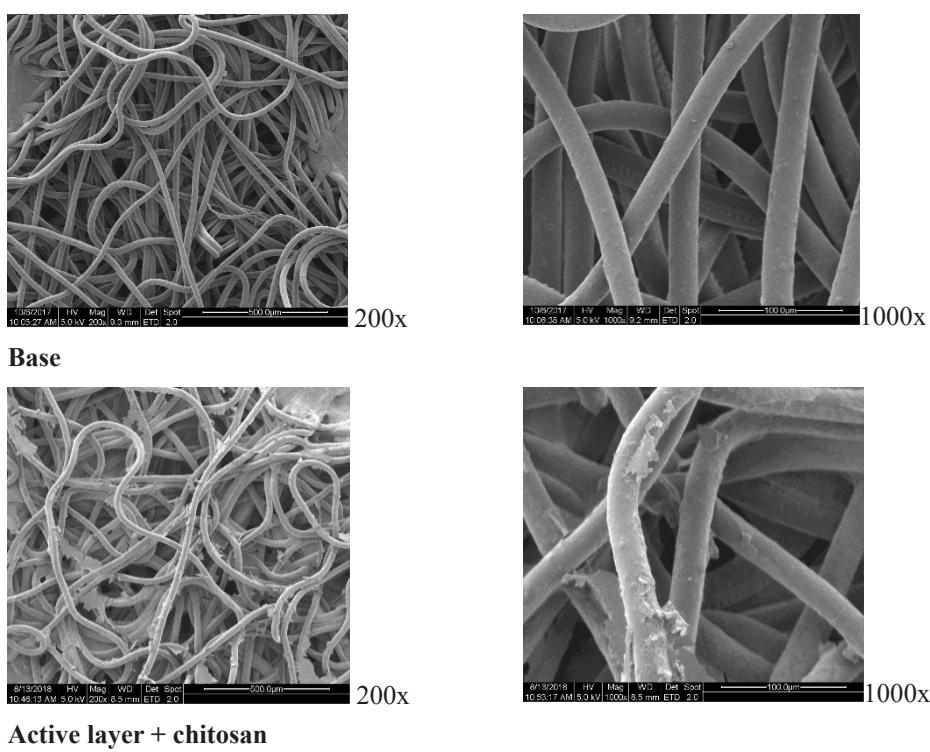


Figure 11. Scanning electron micrographs of the base nonwoven fabric with and without an active layer enriched with chitosan

4. Conclusions

The synthetic process employed in this experiment generated a polymer with appropriate thermal and rheological properties, enabling its processing into nonwoven fabrics using spunbonding. The obtained base nonwoven fabric was characterized by good surface uniformity and relatively low strength, but with notable elongation in the longitudinal and transverse directions. The addition of chitosan lactate significantly improved the mechanical properties of the nonwoven substrate. The base nonwoven fabric with and without an active layer (with and without chitosan lactate) exhibited very

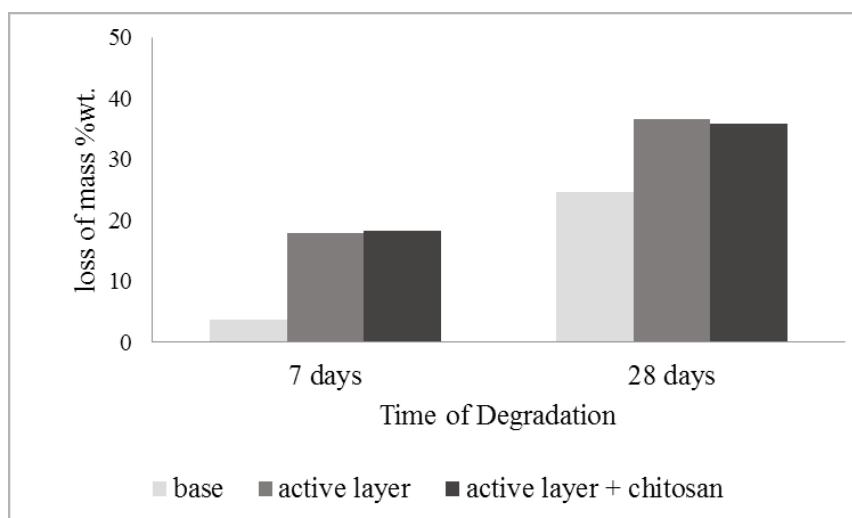


Figure 12. Weight loss for the base nonwoven fabric with and without an active layer in compost medium.

good drapability, which is a particularly desirable feature for cosmetic use, e.g. for face masks. Polyester fibres are hydrophobic. Pure polyester fibres have very low hygroscopicity, which means an absorption of not more than 0.4% moisture under normal conditions. For this reason, the base nonwoven fabric had a very low liquid absorption capacity of 1.54%. However, after application of active substances, the liquid absorption capacity increased to approximately 13%. Chitosan lactate in the active layer inhibited the growth of microorganisms (*S. aureus*) and decreased the pH of the aqueous extract to 4.7, which corresponds to the natural pH of the skin (pH 3.5–5.5). At higher pH values, bacterial infections are more likely; therefore, the obtained value could be very beneficial for cosmetic application. In the extracts of the base nonwoven fabric with and without an active layer, the heavy metal content was below the AAS limit of detection, which is important in the case of cosmetic/hygiene products. Active substances significantly increased the weight loss of the nonwoven fabric during biodegradation in a compost environment; the addition of chitosan to the active layer did not change the dynamics of weight loss of the sample over time. The developed technology enabled the production of a good fibrous base for natural active ingredients that can freely migrate to the extractant (water) during potential use. The obtained material has the potential to be used in the cosmetic industry for the construction of a face masks.

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6. References

- [1] Communication from The Commission to The European Parliament, The Council, The European Economic and Social Committee and The Committee of the Regions.

- A European Strategy for Plastics in a Circular Economy. Brussels, (16.01.2018) COM (2018) 28 final: EUROPEAN COMMISSION.
- [2] Latańska I, Kożera-Żywczak A, Paluchowska E.B, Owczarek W, Kaszuba A, Noweta M, Tazbir J, Kolesinska B, Draczyński Z, Sujka W; (2019). Characteristic Features of Wound Dressings Based on Butyric-Acetic Chitin Copolyesters - Results of Clinical Trials. *Materials* **DOI:** 10.3390/ma12244170.
 - [3] Kucharska M, Sikora M, Brzoza-Malczewska K, Owczarek M; (2019) Antimicrobial Properties of Chitin and Chitosan" – „Chitin and Chitosan: Properties and Applications" Wiley Renewable Resources **DOI:** 10.1002/9781119450467.ch7.
 - [4] Kaczmarek M, Struszczak-Swita K, Li Xi, Szczęsna-Antczak M, Daroch M; (2019) Enzymatic Modifications of Chitin, Chitosan, and Chitooligosaccharides. *Front. Bioeng. Biotechnol.* **DOI:** 10.3389/fbioe.2019.00243.
 - [5] Wiśniewska-Wrona M. El Fray M; (2018) Functional three-component polymeric biocomposites for the treatment of bedsores. *Progress on Chemistry and Application of Chitin and its Derivatives* **DOI:** 10.15259/PCACD.23.19.
 - [6] Ahmad M, Manzoor K, Singh S, Ikram S; (2017) Chitosan centered bionanocomposites for medical specialty and curative applications: A review. *International Journal of Pharmaceutics* **DOI:** 10.1016/j.ijpharm.2017.06.079.
 - [7] Ahmed S, Annu; Ali A; Sheikh J; (2018) A review on chitosan centred scaffolds and their applications in tissue engineering. *International Journal of Biological Macromolecules* **DOI:** 10.1016/j.ijbiomac.2018.04.176.
 - [8] Alves NM, Mano JF; (2008) Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. *International Journal of Biological Macromolecules* **DOI:** 10.1016/j.ijbiomac.2008.09.007.
 - [9] Sujka,W, Draczynski Z, Kolesinska B, Latanska I, Jastrzebski Z, Rybak Z, Zywicka B; (2019) Influence of Porous Dressings Based on Butyric-Acetic Chitin Co-Polymer on Biological Processes In Vitro and In Vivo. *Materials* **DOI:** 10.3390/ma12060970.
 - [10] Zielińska D, Struszczak MH, Madej-Kielbik L, Chmal-Fudali E, Kucharska M, Wisniewska-Wrona M, Brzoza-Malczewska K; (2017) Design of New-Generation Usable Forms of Topical Haemostatic Agents Containing Chitosan. *Molecules* **DOI:** 10.3390/molecules22122240:.
 - [11] Kopania E, Wisniewska-Wrona M; (2016) Biopolymer composites based on lignin and microcrystalline chitosan. *Progress on Chemistry and Application of Chitin and its Derivatives* **DOI:** 10.15259/PCACD.21.13
 - [12] Saad B.Q, Muhammad S.Z, Shariq N, Zohaib K, Altaf H.S, Shehriar H, Ihtesham U.R; (2018) Electrospinning of Chitosan-Based Solutions for Tissue Engineering and Regenerative Medicine. *Int. J. Mol. Sci* **DOI:** 10.3390/ijms19020407.
 - [13] Nagai T, Sawayanagi Y, Nambu N, (1984) Application of chitin and chitosan pharmaceutical preparations. Zikakis JP (ed) Chitin, chitosan, and related enzymes. Academic Press, Inc, Part I, 21–40.
 - [14] Felt O, Nuri P, Gurny R; (1998) Chitosan: a unique polysaccharide for drug delivery. *Drug Dev Ind Pharm* **DOI:** 10.3109/03639049809089942.
 - [15] Bernkop-Schnürch A, Dünnhaupt S, (2012) Chitosan-based drug delivery. *Eur J Pharm Biopharm* **DOI:** 10.1016/j.ejpb.2012.04.007.
 - [16] Gzyra-Jagiela K, Jozwicka J, Gutowska A, Palys B, Kazmierczak D; (2016) Chitosan-Modified Cellulosic Nonwoven for Application in Gynecology. Impact of the Modification Upon Chemical Purity, Structure and Antibacterial Properties. *Fibres and Textiles in Eastern Europe* **DOI:** 10.5604/12303666.1226224.

- [17] Morin-Crini N, Lichtfouse E, Torri G, Crini G, Applications of chitosan in food, pharmaceuticals, medicine, cosmetics, agriculture, textiles, pulp and paper, biotechnology, and environmental chemistry; (2019) Environmental Chemistry Letters **DOI:** 10.1007/s10311-019-00904-x.
- [18] Bashari A, Rouhani Shirvan A, Shakeri M; (2018) Cellulose-based hydrogels for personal care products. Polym Adv Technol. **DOI:** 10.1002/pat.4290.
- [19] Shakeri-Zadeh A, Bashari A, Kamrava SK, Ghalehbashi S; (2016) The use of hydrogel/silver nanoparticle system for preparation of new type of feminine tampons. BioNanoSci. **DOI:** 10.1007/s12668-016-0220-2.
- [20] Costa R, Santos L, (2017) Delivery systems for cosmetics—from manufacturing to the skin of natural antioxidants. Powder Technol **DOI:** 10.1016/j.powtec.2017.07.086.
- [21] Senevirathne M, Ahn CB, Kim SK, Je JY; (2012) Cosmeceutical applications of chitosan and its derivatives. In: Kim SK (ed) Marine cosmeceuticals. Trends and prospects. CRC Press, Taylor & Francis Group LLC, Boca Raton, Chapter 13:169–179, ISBN 9781439860281.
- [22] Chalongsuk R, Sribundit N, (2013) Usage of chitosan in Thai pharmaceutical and cosmetic industries. Silpakorn U Sci Tech J 7:49–53.
- [23] Lipiński Ł, Report on the cosmetic branch in Poland; (2017) 15 years of development.
- [24] Munoz L.P., A, Baez A.G, McKinney D, Garelick H; (2018) Characterization of “Flushable” and “Non- Flushable” Commercial Wet Wipes Using MicroRaman, FTIR Spectroscopy and Fluorescence Microscopy. Environmental Science and Pollution Research 25:20268–20279
- [25] Fibrous raw materials for the production of hygienic papers (2014), Przegląd Papierniczy 3 (in Polish)
- [26] Janiš R; (2017) Comparison of metrological techniques for evaluation of the impact of a cosmetic product containing hyaluronic acid on the properties of skin surface. Biointerphases **DOI:** 10.1116/1.4985696.
- [27] Sionkowska A, Kaczmarek B, Michalska M, Lewandowska K, Grabska S; (2017) Preparation and characterization of collagen/chitosan/hyaluronic acid thin films for application in hair care cosmetics. Pure Appl. Chem. **DOI:** 0.1515/pac-2017-0314.
- [28] P 397 460 S. Dutkiewicz, T. Fiszer, Z. Młodzikowski, A. Niekraszewicz, J. Wesołowski, D. Chojnacki „Method for producing the aliphatic – aromatic copolyester with improved colours”.
- [29] Olejnik A, Gościnańska J, Nowak I; (2012) The importance of hyaluronic acid in the cosmetics industry and aesthetic medicine, CHEMIK 66; 2, 129-135 (in Polish)
- [30] Jurzak M, Włodarska K, Garncarczyk A, Gojniczek K; (2008) Hyaluronic acid – a multidirectional glycosaminoglycan. Dermatologia estetyczna 10;4 (in Polish)
- [31] Tomaszewicz V, Klawe J.J, Szady-Grad M, Chrzanowska M; (2015) Selected methods of testing the effectiveness of collagen in relation to the condition of the hair and skin. Scientific and Methodical Review 29, VIII; 4 (in Polish)
- [32] Clarke S; (2008) Essential Chemistry for Atomatherapy. Churchill Livingstone Elsevier; ISBN: 978-0-4431-0403-9
- [33] PN-EN ISO 139:2006: „Textiles-Standard atmospheres for conditioning and testing”.
- [34] PN-EN 29073-1:1994 Textiles – Testing of nonwoven. Estimation of surface density.
- [35] PN-EN 29073-3:1994 Textiles. Methods of nonwoven testing . Estimation of tenacity and elongation.
- [36] PN-EN ISO 9073-7:2011 Textiles- Testing of nonwoven- Part7: Estimation of bending length.

- [37] PN-EN ISO 9073-6 Textiles- Testing of nonwoven. Part 6: Absorption.
- [38] PN-EN ISO 20743:2013 Textiles –Determination of antibacterial activity of textile products.
- [39] PN-EN ISO 10993-12:2009:“Biological assessment of medical devices-Part 12: Preparation of the sample and reference materials”.
- [40] The United States Pharmacopeia (2015) USP 38 NF 33.
- [41] PN-EN ISO 3071:2007: “Textiles. Determination of pH of aqueous extract”.
- [42] European Pharmacopoeia-8th Edition volume I 01/2014 2.2 Psychical and physicochemical methods.
- [43] PN-P-04781/06:1988: “Textile medical materials. Determination of water soluble matter”.
- [44] PN-EN 14045:2005 Packaging –Assessment of the decomposition of packaging materials in laboratory scale in compost conditions.
- [45] PN-EN 14806:2010 Packaging –Introductory assessment of the decomposition of packaging materials in laboratory scale in compost conditions.
- [46] PN-EN ISO 20200:20016-01 Polymers –Estimation of polymer decomposition in laboratory scale in simulated compost conditions.