NONWOVEN CHITOSAN - PREPARATION AND PROPERTIES

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Abstract:

This article focuses on preliminary investigations of the manufacture of nonwoven chitosan from a 38-mm chitosan staple fibre and fibres containing silver nanoparticles. The nonwoven chitosan is built of several needle-punched layers of fleece, with a lengthwise arrangement of chitosan fibres. Estimated were mechanical and sorption properties, apparent density, thickness and air permeability of the nonwoven chitosan.

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1. Introduction

Fibrous forms of chitosan, such as nano- and microfibers, staple fibres, and yarns, have been used widely in several application, especially medicine [1–4]. These fibrous forms are frequently modified or functionalized by the addition of multi-wall carbon nanotubes, nanoparticles of various metals, calcium phosphate, collagen, fibroin, or keratin [4–12]. The chitosan fibres was applied in the preparation of semi-absorbable surgical meshes, chitosan knitted fabrics, and prostheses of nerves [4,13–15].

Chitosan–metal complexes reveal enhanced antibacterial activity when compared with virgin chitosan. Silver nanoparticles penetrate the walls of *Escherichia coli* and *Staphylococcus aureus* cells [16–18]. Pure chitosan yarns have been applied in the construction of knitted fabrics for use in textile scaffolds [19,20].

The main objective of this work was to assess the suitability of chitosan fibres in the preparation of nonwoven chitosan. For investigative purposes, a staple fibre of chitosan was prepared with the addition of silver nanoparticles (**Table 1**). An assessment of the antibacterial activity of the nanoparticle-functionalized staple fibre of chitosan was conducted, which was aimed at preparing needle-punched nonwoven chitosan from the layers of chitosan fibre fleece. The nonwoven were characterized by tenacity and extension, sorption properties, apparent density, surface density, thickness, and air permeability.

2. Materials and Methods

2.1. Materials

Chitosan fibres and nanoparticle-modified chitosan fibres were spun on a spinning line at Institute of Biopolymers and Chemical Fibres (IBWCh). Staple fibres were prepared by cutting a wet fibre bundle into pieces, 38 mm long, with linear density of 2.24 dtex of the elemental fibres, followed by unstressed drying. The obtained chitosan fibres (Table 1.) contained nanoparticles of silver. The silver nanoparticles were added to the chitosan spinning dope. The following nanoparticles were used in the investigation: silver nanoparticles (Hydrosilver 1000 delivered by Amepox Co, Poland).

Table 1. Characteristics of chitosan staple fibre

Fibre symbol	Kind of nanoparticles	Concentration of nanoparticles (mg/kg)
FChit-P1	Without nanoparticles	0
FChit-P2	Silver nanoparticles	53.1

2.2. Methods

2.2.1. Preparation of Chitosan Nonwoven

The production line (Asselin Co), composed of a carding machine and a needle punching loom was employed to prepare the nonwoven from chitosan staple fibre. First, an elemental fleece was prepared which was then overlaid one on the other (5 or 10 single fleeces in one final product). The fibres were arranged longitudinally on the web which was one-sided, passage-wise, punched with needles 15×18×40×3.5 RB to a constant depth of 12 mm and a needling density of 30/cm^2.

Mechanical properties of chitosan fibre were tested according to standards: PN-ISO-1973:2011 and PN-EN ISO 5075:1999. Measurements: at RH of 65±4% and at a temperature of 20±2 ^{o}C.

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Antibacterial activity of the chitosan fibre against *Staphylococcus aureus* ATTC 6538 and *Escherichia coli*, was estimated using the quantitative test, according to standard JIS L 1902:2002. The number of live bacteria growing in the tested fibre sample and in a standard substrate (regular chitosan fibre) was determined after 24-hours of incubation.

Silver content was determined directly in a mineralized sample by the Flame Atomic Absorption Spectrometry (FAAS) at wavelength of 328.1 nm. The fibre was first incinerated at 575 ºC and then, mineralized in a 75% HNO_3 in a microwave oven. SCAN-1 atomic absorption spectrometer (Thermo Jarrell Ash Co.) was used in the analysis. The background was corrected using the Smith-Hiettje method [21].

Content of other nanoparticles in the fibre was not determined; content values are given as weighted.

2.2.2. Estimation of the Physical Properties of the Chitosan Nonwoven

Thickness was measured by the thickness gauge, Arthur Meiber KG LTG according to standard PN-EN ISO 5084:1999. A pressure of 2 Pa was applied in the measurements. The surface of 1000 mm^2 was measured. 10 measurements were made to compute an average value with (having an accuracy of 0.01 mm) the variation coefficient.

Surface mass was measured in accordance with the standard PN-EN 29073-1:1994. According to PN-EN ISO 186:2004, about 50,000 mm^2 of a sample was taken from the tested material,. The samples were air-conditioned prior to the measurement of size and weight. The surface mass of the nonwoven was determined with accuracy of up to 0.1% of the weighted mass.

The apparent density is the quotient of the mass of the textile material by its volume, including all voids appearing between the structural elements of the material. Apparent density was estimated in accordance with standard PN-85/P-04688. Measurements were made in three points along the sample and in three points across, with accuracy of 1 mm; thereafter, the thickness of the material was determined according to standard PN-EN ISO 5084:1999 and its mass with accuracy of up to 0.2% of the weighted mass.

Air permeability was measured according to standard PN-EN ISO 9237:1998 by means of the apparatus Textest FX 3300. Measurements were made in 10 points, at distance of 5 cm from the edge, at partial vacuum of 100 Pa and nominal measurement surface of 20 cm^2.

Tenacity and extension of the nonwoven were measured on Instron machine according to standard PN-EN 29073-3:1994.The samples were kept for 24 hours, air-conditioned at 25 ºC and RH of 65%. The rate of the movement speed of the transversal bottom clamp was 100 mm/min, with distance of 200 mm between the clamps, and 50 mm width of the sample. Samples were cut out along and across from the nonwoven.

Sorption of the nonwoven was estimated by means of the sorption meter -SORP 3.

3. Results and Discussion

3.1. Characteristic of Chitosan Staple Fibre

Chitosan fibres and nanoparticles- modified chitosan fibres were prepared on an experimental spinning line at IBWCh, staple fibre for the processing of nonwoven.

Chitosan fibres and nanoparticles of silver containing- chitosan staple fibre with length of 38 mm, were prepared for the manufacture of nonwoven (Table 1.). Two lots

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of staple fibers were made: one without nanoparticles (FChit-P1) and the other with nanoparticles of silver in the amount of 53.1 mg/kg (FChit-P2).
Bacteriostatic and bactericidal activity was examined in selected chitosan staple fibres containing nanoparticles of silver staple fibre. Results are compiled in **Table 2**.

Table 2. Antibacterial activity of silver nanoparticles containing chitosan staple fibres against *Staphylococcus aureus*

Symbol of fibres	Kind of fibres	Time h	No of bacteria, jtk/pr	Bacteriostatic activity	Bactericidal activity	Growth
Chit-0	(standard)	0	3.5×10^{4}	-	-	-
		24	1.3×10^{7}	-	-	2.6
FChit-P2	staple	24	2.0×10^{1}	5.7	3.3	-

Table 3. Antibacterial activity of silver nanoparticles containing chitosan staple fibres against *Escherichia coli*

Symbol of fibre	Kind of fibres	Time h	No of bacteria, jtk/pr	Bacteriostatic activity	Bactericidal activity	Growth
Chit-0	(standard)	0	1.6×10^{5}	-	-	-
		24	1.7×10^{8}	-	-	3.0
FChit-P2	staple	24	2.0×10^{1}	5.7	3.3	-

Bacteriostatic and bactericidal activity against the strains of *Escherichia coli. Staphylococcus aureus* features chitosan fibres having content of nanoparticles of silver 53.1 mg/kg (Table 2 and Table 3). As earlier reported [8], chitosan fibers with silver content are active against both Gram negative and Gram positive bacteria.

Two charges of chitosan staple fibre were prepared: one without nanoparticles (FChit-P1) and the other containing silver nanoparticles (FChit-P2). Mechanical properties of the fibers are presented in Table 4.

Table 4. Mechanical properties of chitosan staple fibre

Parameter		FChit-P1 without nanoparticles	FChit-P2 silver nanoparticles
Linear density	dtex	2.93	2.76
Breaking force of air conditioned	cN	2.12	2.10
Tenacity, air conditioned	cN/tex	7.23	7.60
Elongation at break air conditioned	%	17.0	17.0
Loop tenacity air conditioned	cN/tex	3.05	3.13
Relative loop tenacity	%	42.2	41.2
Initial modulus of elongation	cN/tex	147	204
Fibre diameter	µm	16.5	15.7

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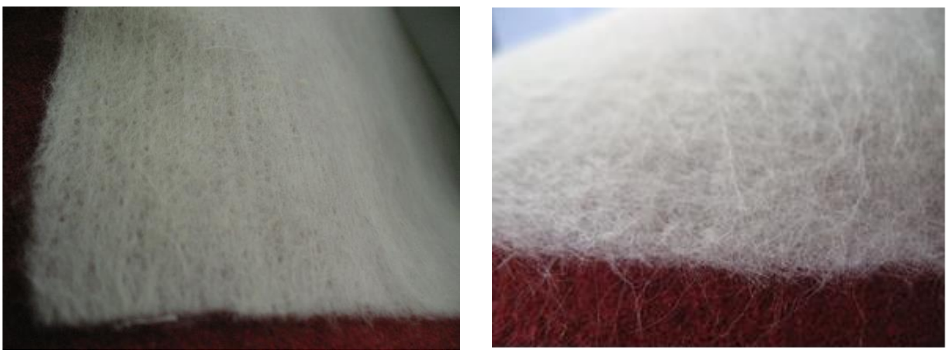
The tenacity of the staple fibres is on the level of 7.23–7.60 cN/tex, with elongation on the level of 17%. Chitosan staple fibres reveal a lower tenacity and higher elongation than the chitosan yarn [13]. The reason for it is to be found in the conditions adopted in the preparation of the staple fibre. They were cut under wet conditions and dried afterwards, in a loose fleece without stress. The presence of the silver nanoparticles does not affect the mechanical properties of the fibre. Diameter of the elemental fibres is at the level of 15-18 microns. Chitosan staple fibres showing a higher loop tenacity (3.13 cN/tex) than chitosan yarn are candidates for the preparation of nonwoven.

3.2. Investigation in the Preparation of Chitosan Nonwoven

Chitosan staple fibre with length of 38 mm and modified by nanoparticles were employed in the preparation of nonwoven on typical textile machinery at the Faculty of Material Technologies and Textile Design, University of Technology, Łódź.

The nonwoven was prepared from chitosan staple fibers: without silver nanoparticles (NWChit-P1) and with silver nanoparticles (NWChit-P2). Two kinds of nonwoven were prepared with varied surface mass, and their physical parameters were measured. Crushing and breaking of the fibre could be observed in the course of the manufacture mainly in the needling step. Static electricity caused repulsion problems.

The technological problems are the reason for the scattering of measurement results.



a b

Figure 1. Image of chitosan of nonwoven marked a) NWChit-P1, b) NWChit-P2.

The images in Figure 1 present longitudinal views of the nonwoven surface. The positive attempts of preparing chitosan nonwoven augur the chance of their manufacture on typical textile machinery. It may be regarded as an achievement since it is the first time that chitosan nonwoven was made from pure chitosan staple fibres.

Physical Properties of Chitosan Nonwoven

Irregularity of thickness was characteristic of the thicker nonwoven NWChit-P1 and NWChit-P2 (Table 5). With 5 fleeces, NWChit-P2 nonwoven, is much thicker than NWChit-P1, prepared at equal technological parameters. The scattering of Mp measurements is to be explained by technological problems, whilst needle-punching static load and crushing of the fibre resulted in repulsion and breaks. Air permeability of the nonwoven is closely related to their apparent density. It was found that with the same needling density, the increasing surface mass causes a decrease of the air permeability.

Table 5. Test results of needle punched chitosan nonwoven

Symbol of nonwoven	Numbers of fleeces in the nonwoven	Thick-ness mm	Surface mass Mp, g/m²	Apparent density kg/m³	Air perme-ability l/m²/s
NWChit-P1 without nanoparticles	5	0.28	29.52	76.11	5010
	10	1.28	97.42	105.41	2390
NWChit-P2 with silver nanoparticles	5	0.43	38.38	71.50	5150
	10	1.27	90.81	89.26	3170

Table 6. Strength and elongation of the needle punched chitosan nonwoven

Nonwoven	Direction of measurement	Numbers of fleeces in the nonwoven	Elongation at break mm	Breaking force N	Young modulus MPa
NWChit-P1	along	5	94.8	0.019	0.038
		10	120.2	0.018	0.073
NWChit-P2		5	95.6	0.023	0.030
		10	120.1	0.020	0.045
NWChit-P1	across	5	185.5	0.031	0.190
		10	169.8	0.092	0.086
NWChit-P2		5	110.6	0.035	0.028
		10	223.2	0.083	0.011

Nonwoven NWChit-P2, drawn in the along direction, are more resistant to break than nonwoven NWChit-P1 (Table 6). Elongation is similar in nonwoven composed of both 5 and 10 fleeces. When drawn across, the highest strength appeared in NWChit-P1, composed of 10 fleeces and the highest elongation in NWChit-P2.

Nonwoven drawn across show generally a much higher strength and elongation at break than those drawn along.

Table 7. Sorption capacity of chitosan nonwoven

Nonwoven	Numbers of fleeces in the nonwoven	Sorption capacity g/g	Standard deviation
NWChit-P1	5	22.64	14.31
NWChit-P2		31.40	18.50
NWChit-P1	10	20.22	4.03
NWChit-P2		25.69	9.25

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Nonwovens of the NWChit-P2 fibre surpass in sorption capacity those made of NWChit-P1. (**Table 7**). Nonwoven made of the same fibre reveal a higher sorption capacity at lower surface mass.

4. Conclusion

Chitosan fibres and modified with nanoparticles of silver were assessed in regard to their suitability in the manufacture of nonwoven using typical industrial equipment. Chitosan staple fibre was applied in the preparation of nonwoven. Nanoparticles of silver proved to be the right additive to chitosan fibres, conferring enhanced bacteriostatic and bactericidal properties upon the fibre. The fibre, bearing such properties, is a promising material for medical uses like wound dressings. To achieve this purpose, it needs to be processed to textile forms, like nonwoven. Attempts to prepare nonwoven materials from the chitosan fibres produced positive results. It must be, however, admitted that the processes did not run smoothly, thereby, revealing serious inadequate properties of the processed fibres, like low tenacity and elongation, poor quality of the staple fibres and high static electricity on the fibre which, in consequence, has led to defects in the prepared chitosan nonwoven.

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