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Time-of-flight secondary ion mass spectrometry analysis of chitosan-treated viscose fibres

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ABSTRACT

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed to analyse cellulose viscose fibres treated with different chitosan-based solutions. The analysis reports several new features in the TOF-SIMS spectra for systems with various forms of chitosan-treated surfaces. The characteristic positive ion TOF-SIMS signals for chitosan are reported at *m/z* 147.90, 207.07, and 221.09, and characteristic signals for trimethyl chitosan are present at *m/z* 58.03 and 102.09. Furthermore, new fragments were suggested to characterise acetylated chitosan molecules. The relative surface concentrations of different species were obtained based on the specific signal ratios (originating from a specific fragment and cellulose). SIMS imaging was then performed in order to investigate the surface distribution of chitosan, trimethyl chitosan, and Na-containing nanoparticles. In order to perform TOF-SIMS imaging, the above-mentioned characteristic signals were employed and *m/z* 22.99 was used for Na nanoparticles.

Introduction

Natural cellulose-based fibres are increasingly gaining attention in the engineering of composite materials with a special emphasis on their antimicrobial properties. Viscose rayon is a fibre made of partially depolymerised cellulose from woody material by successive treatment with CS_2, NaOH, and H_2SO_4 resulting in shorter and softer fibres that are more suitable for biomedical applications [1–3]. Regarding the surface modification of cellulose fibres to introduce antimicrobial properties, natural bioactive compounds are deemed to be the most attractive, eco-friendly alternative to synthetic antimicrobial agents. The latter is especially important for applications in cosmetics, medicine, and health care, as these types of materials need to be safe, non-toxic, and skin friendly [1,2,4].

Among the various bioactive compounds, cationic polysacharrides show promise in biomedical applications due to their antimicrobial activity. One of the most popular amino polysaccharides is chitosan, which is obtained by alkaline deacetylation of chitin. Chitosan's positive charge, the degree of N-deacetylation, the mean polymerisation degree, and the nature of the chemical modifications are the properties that strongly influence its antimicrobial effectiveness [1,2,4]. It is used as a natural antimicrobial agent for the development of new medical products and is gaining in popularity as the FDA has approved it as a food ingredient. Besides its antimicrobial activity, it exhibits anti-cholesterolemic, anti-ulcer, anti-uremic, and anti-tumour effects [5]. A wide variety of chitosan derivatives are synthesised due to the limited solubility of commercial chitosan. Among the most promising ones are quarternised chitosan, carboxymethylated chitosan, and tiol–chitosan, which have found applications as matrixes for the preparation of several medical materials in different forms and for different purposes [6]. Chitosan has already been extensively studied as an active surface agent integrated into textile fibres to produce advanced sanitary products and medical devices [1,2,4]. The latest trend is to design chitosan nanoparticles that can be reversibly or irreversibly attached onto cellulose material. The high specific area due to their nano size as well as the manipulation of the bonding may increase the bioactive properties of fibres functionalised by chitosan nanoparticles [7,8]. It was shown in our previous work that chitosan nanoparticles have a high antibacterial function with important applications, e.g. as viscose tampon coatings that inhibit the pathogens causing toxic vaginal infections. It has also been shown that chitosan nanoparticles attached onto viscose fibres may also act as a novel vaginal drug delivery system for local

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Table 1
Characteristic fragments for specific compounds.

compound	*m/z* signal
$C_6H_7O_3^+$ (hexose monomer)	127.04, 145.05
ethylene glycol monostrearate	283.26 (-CH_2CH_2OH) and 311.30 (-OH)
different hydrocarbons separated by *m/z* 16 or 28	675, 659, 631, 615, 587, 571, 543, 527, 499, 483, 455, 437, and 387
CH_4N^+	30.03
Na	22.99
NH_4^+	18.03
from chitosan	
$C_4H_{21}N_{14}O$ (from chitosan) → $C_4H_{23}N_{14}O$ (from chitosan)	281.20 → 283.22
acetylated chitosan	221.09 and 207.07
$C_8H_{13}NO_5$ chitin monomer from chitosan	203.08
$C_6H_{13}NO_5$ glucosamine fragment from chitosan	179.08
$C_6H_{11}NO_4$ glucosamine fragment from chitosan	161.07
chitosan fragment	147.90
$C_6H_{10}NO_3^+$ (from the glucosamine monomer)	144.07
$C_5H_{12}NO^+$ from trimethylchitosan	102.09
$C_3H_9N^+$ from trimethylchitosan	59.07
$C_2H_4NO^+$ from chitosan	58.03

administration of microbiocids or other therapeutic drugs/vaccines [7]. Due to their beneficial bioactive properties, chitosan in different structural forms also has implications for modifying and testing many other medical devices (vascular grafts, catheters, wound dressings, hernia meshes, etc.) and material surfaces, due to which its use as a functional coating is of crucial importance [5].

The success of cellulose functionalisation and applications, especially in the case of medical textiles, depends strongly on their surface properties; i.e. the physics and chemistry of the fibre/fabric surface strongly influence their interaction with the chosen environment. The surface of antimicrobial functionalised fibres is responsible for the interaction with microorganisms, thus, the development and optimisation of many functional medical textiles require detailed knowledge of the chemical and physical microstructure of the surface. This knowledge plays a central role in understanding process – surface structure – property relationships, which are crucial parameters in the enhancement or suppression of the efficiency of functionalised fibres regarding bacteria and fungi inhibition. It should be noted that the bonding mechanism of coatings with correlations in surface chemistry changes and the further influence of surface parameters on medical device surface bio-efficiency are not yet clearly or fully understood. Thus, besides developing novel multifunctional natural coatings for cellulose fibres, achieving a deep understanding of the surface composition of functionalised fibres is also a great challenge.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a surface-sensitive analytical method. It is a powerful technique for analysing and directly mapping chemical components on the surfaces of solid samples [9–15]. In combination with a ToF analyser, ToF-SIMS provides several advantages compared with other mass spectrometric and surface-sensitive techniques. For example, a wide mass range can be analysed (0–10000 atomic mass units); it has a high mass to charge ratio (*m/z*) resolution > 10000, and it is possible to reconstruct any image area in order to obtain information about a specific fragment [16–23].

Hitherto, to the best of our knowledge, no TOF-SIMS analysis of viscose fibres functionalised by chitosan and chitosan nanoparticle has been reported. Furthermore, herein, new SIMS fragments are reported to characterise specific components.

Experimental

Viscose fibres functionalised by chitosan and chitosan nanoparticles adsorbed onto viscose fibres at variable pH values were analysed by the ToF-SIMS technique. In this research, chitosan (CS) and trimethyl chitosan (TMC) nanoparticle dispersions were used as cellulose fibre coatings and compared with CS solutions coated on the fibre. Chitosan adsorption (in solution and nanoparticle form) onto fibres was performed at pH values of 4 and 7 in order to investigate the influence of different pH values on chitosan macromolecule conformation and, consequently, on its adsorption ability.

Materials

CS (M = 82000 g/mol, degree of deacetylation 77.4%) and TMC (M = 90000 g/mol, degree of trimethylation 66%) were supplied by Kitozyme, Herstal, Belgium. Chitosan powder was suspended in ultrapure water (with a resistivity of 18.2 MΩ, obtained from Milli-Q, Millipore Corporation, Massachusetts, USA) in order to prepare 0.5% (*w/V*) solution. The solution was stirred continuously while lactic acid (concentrated) was added dropwise to enable the dissolution of chitosan. Afterwards, the solution was left stirring overnight and the pH was adjusted with lactic acid to 4.0 prior to further usage.

Dissolution of TMC was achieved by suspending TMC powder in ultrapure water. The solution was left stirring overnight. Since TMC is water-soluble, lactic acid was added only to adjust the pH to 4.0. The pH value of both CS and TMC solutions was also adjusted to 7 (with 0.1 M NaOH) before being applied as a fibre coating. The same preparation procedure has been employed previously [7,24].

Chitosan nanoparticles were prepared by the ionic gelation

Table 2
Sample preparation with corresponding abbreviations.

Sample abbreviation	Description
CV	Viscose fibres (without CS treatment – untreated sample, cellulose base).
CS-R4	CV treated with 0.5% (w/v) CS solution at pH 4; medical grade CS was used with M = 82000 g/mol, degree of deacetylation – DDA = 77.6%; the pH was adjusted with concentrated lactic acid.
CS-R7	CV treated with 0.5% (w/v) CS solution at pH 7; medical grade CS, M = 82000 g/mol, DDA = 77.6%; the pH was adjusted with 0.1 M NaOH solution.
CSNP4	CV treated with chitosan nanoparticles (CSNP) dispersion, synthesised by ionic gelation between CS and sodium tripolyphosphate using a mass ratio of 5:1 (CS:TPP); the pH of the CSNP dispersion was 4 (adjusted with concentrated lactic acid).
CSNP7	CV treated with CSNP, synthesised by ionic gelation between CS and sodium tripolyphosphate using a mass ratio of 5:1 (CS:TPP); the pH of the CSNP dispersion was 7 (adjusted with 0.1 M NaOH).
TMC-R4	CV treated with 0.5% (w/v) TMC solution, pH 4; medical grade TMC, M = 90000 g/mol, degree of substitution – DS = 64%; the pH was adjusted with concentrated lactic acid.
TMC-R7	CV treated with TMC solution, c = 0.5% (w/v), pH 7; medical grade TMC, M = 90000 g/mol, degree of substitution – DS = 64%; the pH was adjusted with 0.1 M NaOH solution.
TMCNP4	CV treated with a trimethyl chitosan nanoparticle (TMCNP) dispersion at pH 4; particles were synthesised using TPP with a 5:1 TMC:TPP mass ratio; the pH was adjusted with concentrated lactic acid.
TMCNP7	CV treated with a trimethyl chitosan nanoparticle (TMCNP) dispersion at pH 7; particles were synthesised using TPP with a 5:1 TMC:TPP mass ratio; the pH was adjusted with 0.1 M NaOH.