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 CS₂, NaOH, and H₂SO₄ 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 polysaccharides 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 thiol-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	<i>m/z</i> signal
C ₆ H ₇ O ₃ ⁺ (hexose monomer)	127.04, 145.05
ethylene glycol monostearate	283.26 (-CH ₂ CH ₂ OH) and 311.30 (-OH)
different hydrocarbons separated by <i>m/z</i> 16 or 28	675, 659, 631, 615, 587, 571, 543, 527, 499, 483, 455, 437, and 387
CH ₄ N ⁺	30.03
Na	22.99
NH ₄ ⁺	18.03
from chitosan	
C ₄ H ₂₁ N ₁₄ O (from chitosan) → C ₄ H ₂₃ N ₁₄ O (from chitosan)	281.20 → 283.22
acetylated chitosan	221.09 and 207.07
C ₈ H ₁₃ NO ₅ chitin monomer from chitosan	203.08
C ₆ H ₁₃ NO ₅ glucosamine fragment from chitosan	179.08
C ₆ H ₁₁ NO ₄ glucosamine fragment from chitosan	161.07
chitosan fragment	147.90
C ₆ H ₁₀ NO ₃ ⁺ (from the glucosamine monomer)	144.07
C ₅ H ₁₂ NO ⁺ from trimethylchitosan	102.09
C ₃ H ₉ N ⁺ from trimethylchitosan	59.07
C ₂ H ₄ NO ⁺ from chitosan	58.03

administration of microbicides 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% (<i>w/v</i>) CS solution at pH 4; medical grade CS was used with <i>M</i> = 82000 g/mol, degree of deacetylation – DDA = 77.6%; the pH was adjusted with concentrated lactic acid.
CS-R7	CV treated with 0.5% (<i>w/v</i>) CS solution at pH 7; medical grade CS, <i>M</i> = 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% (<i>w/v</i>) TMC solution, pH 4; medical grade TMC, <i>M</i> = 90000 g/mol, degree of substitution – DS = 64%; the pH was adjusted with concentrated lactic acid.
TMC-R7	CV treated with TMC solution, <i>c</i> = 0.5% (<i>w/v</i>), pH 7; medical grade TMC, <i>M</i> = 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.

Fig. 1. Structures of the different components analysed with ToF-SIMS.

technique, as discussed in detail previously [7,25]. Regenerated cellulose fibres, pure and highly absorbent, in the form of a tampon band composed of two types of fibres, Lenzing Viscose® and Lenzing Viscostar®, mixed at a 70–30% ratio, were chosen as a base material for the

adsorption of chitosan solutions and chitosan nanoparticle dispersions.

Fig. 2. The positive ion ToF-SIMS spectrum in the m/z range of 140–400 measured for the CS-R4 sample.

Fig. 3. The positive ion ToF-SIMS spectrum in the m/z range of 140–400 measured for the CS-R7 sample.

Fig. 4. Suggested fragmentation of glucosamine [35].

Functionalisation of viscose cellulose fibres

Fibres were treated by aqueous CS solutions or nanoparticle dispersion by an impregnation procedure. Impregnation was carried out at room temperature for a period of 30 min at a wet pickup of 80–100% with the help of a two-roller foulard (pressure 2 bar, passage of the material 2 m/min). Samples were dried at 40 °C for 30 min in a laboratory oven. The fibres were subsequently conditioned before being analysed further [7,24].

Different coating procedures resulted in 8 differently treated fibre samples, whose designations are presented in Table 2 (an untreated reference sample is also included).

ToF-SIMS technique

Secondary ion mass spectra were acquired using a Physical Electronics ToF-SIMS TRIFT II spectrometer equipped with a primary ion gun that produces a beam of $^{69}\text{Ga}^+$ ion source. Measurements were performed at an acceleration voltage of 25 kV for 7 min, in positive ion mode. Spectra were collected in the m/z ratio range between 2 and 4000. At least three different areas were analysed on each sample in order to check for reproducibility, and representative spectra were reported. Charge compensation was performed with an electron flood gun pulsed out of phase with respect to the ion gun. The spectra were calibrated using the hydrocarbon fragments CH^+ , C_2H_3^+ , C_3H_5^+ , and

Fig. 5. The positive ion ToF-SIMS spectrum (m/z range 10–700) for the TMC-R7 sample.

Table 3

The signal intensity ratios of the mass peak at m/z 147.90, 102.09, or 58.03 relative to the mass peak at m/z 127.04 (the standard deviations calculated from 3 measurements are given in brackets).

Sample	147.90/127.04 (counts/counts)	102.09/127.04 (counts/counts)	58.03/127.04 (counts/counts)
CV	0.38 (0.01)	0.37 (0.10)	3.09 (1.20)
CS-R4	4.00 (1.98)		
CS-R7	0.77 (0.14)		
CSNP4	0.76 (0.50)		
CSNP7	0.60 (0.14)		
TMC-R4		17.89 (1.44)	60.08 (6.29)
TMC-R7		23.60 (2.13)	74.91 (13.3)
TMCNP4		5.15 (0.86)	16.78 (3.28)
TMCNP7		25.02 (5.52)	81.45 (13.99)

$C_7H_7^+$. The mass resolution ($m/\Delta m$) of the SIMS instrument was approx. 10 000.

Results and discussion

Description of the untreated viscose fibres

Table 1 and Fig. 1 summarise the characteristic signals that were obtained and the components investigated in this study. The characteristic m/z peaks of the hexose monomer at m/z 127.04 ($C_6H_7O_3^+$) and 145.05 ($C_6H_9O_4^+$) were detected for the CV sample (untreated viscose fibres – used as a reference). However, these signals were not

intense – with a relative intensity (rel. int.) of 15% and 17%, respectively (the spectrum is not shown herein). Moreover, mass peaks at m/z 283 (a group of signals at m/z 281, 282, 283, 284, and 285) and at m/z 311 (a group of signals at m/z 309, 310, 311, 312, and 313) were also present in the spectrum for the CV sample. They most likely originate from ethylene glycol monostearate [26,27], which is an additive for a viscose formulation. In the high m/z region (above 350), intense mass peaks that would describe cellulose were not detected (due to intense fragmentation).

Furthermore, intense peaks separated by 16 or 28 m/z units were detected at m/z 675 $\rightarrow$ m/z 659 $\rightarrow$ m/z 631 $\rightarrow$ m/z 615 $\rightarrow$ m/z 587 $\rightarrow$ m/z 571 $\rightarrow$ m/z 543 $\rightarrow$ m/z 527 $\rightarrow$ m/z 499 $\rightarrow$ m/z 483 (a fragment at m/z 481 was also detected) $\rightarrow$ m/z 455 $\rightarrow$ m/z 437 $\rightarrow$ m/z 387. Masses separated by 16 or 28 m/z units, as present for the latter case, indicate cleavages of hydrocarbon fragments CH_3 or C_2H_4 (a minor deviation from the 16 or 28 units indicates the presence of other fragment isotopes). The occurrence of hydrocarbons on the viscose fibres is most likely due to surface contamination by some long-chain polymers on top of the viscose polymer. The probable origin of contamination is due to the viscose spinning process, where surfactants and lubricants are added [26]. It is also possible that adventitious carbon species adsorbed on the surface after the sample preparation procedure and transferred to the spectrometer [28,29], although this surface contamination does not usually have such a high molecular mass.

CS solution-treated samples (CS-R4 and CS-R7)

The purpose of this analysis is to demonstrate that CS was adsorbed

CS-R4 sample

CS-R7 sample

CSNP4 sample

CSNP7 sample

(caption on next page)

Fig. 6. Total ion image (left images) and mapping of the mass fragments at m/z 147.90, 207.07, and 221.09 on the surface of the CS-treated samples (right images). The scale bar is 10 μm .

on the CV sample from the CS-containing solutions at pH 4 and 7. Moreover, the influence of different pH values on CS macromolecule conformation and, consequently, on its adsorption ability, was investigated. As both samples were treated with CS, peaks at m/z 18.03 and m/z 30.03 are expected due to NH_4^+ and CH_4N^+ fragments [30], respectively. However, for both CS-R4 and CS-R7 these peaks had low intensity – the rel. ints. were 13% and 15% for the m/z 18.03 signal and 14% and 16% for the m/z 30.03 signal, respectively.

Figs. 2 and 3 show a characteristic segment of the positive ion ToF-SIMS spectra measured for CS-R4 sample. The low m/z region did not differ significantly from the spectrum of the reference CV viscose fibres as the same base material was employed. In the higher m/z region, the CS-R4 sample spectrum shows intense peaks at m/z 147.90, 207.07, 221.09, 281.20 and 283.22. The signals at m/z 207.07 and 221.09 most likely originate from acetylated CS [30,31] (the fragments $\text{C}_7\text{H}_{13}\text{NO}_6$ and $\text{C}_8\text{H}_{15}\text{NO}_6$ originate from acetylglucosamine due to acetylated chitosan). The fragment at m/z 281.20 has been ascribed previously to $\text{C}_4\text{H}_{21}\text{N}_4\text{O}$, which originates from CS [30–33]. However, how this fragment is formed from CS is currently not clear. A peak at m/z 147 was also reported previously to be characteristic of chitosan [30,34]. The peak at m/z 281.20 was detected in the spectrum of the CS-R4 and CS-R7 samples as a part of a strong group of relatively broad peaks around m/z 283 (the highest peak was at m/z 283.22, rel. int. 62%), which could represent a group of the same molecular fragments composed of different isotopes. However, the peak at m/z 283, together with the signal at m/z 311, could also originate from ethylene glycol monostearate in the base viscose fibre, as explained above. This peak pair (at m/z 283 and 311) was detected with an intense signal (always with the rel. int. above 50%, apart from TMC, for which it was lower than 6%) in all the measured samples, including the CV reference, as mentioned above.

The fragmentation of CS or acetylated CS using ToF-SIMS has not been studied or published in detail yet. Possible fragments built from the glucosamine monomer or chitin monomer could be speculated. A peak at m/z 144.07 was detected (but was not intense, with a rel. int. of 15%), possibly originating from $\text{C}_6\text{H}_{10}\text{NO}_3^+$ (from the glucosamine monomer after the cleavage of two $-\text{OH}$ groups [35]). On the other hand, signals referring to glucosamine fragments from deacetylated CS, i.e. $\text{C}_6\text{H}_{13}\text{NO}_5$ at m/z 179.08 or $\text{C}_6\text{H}_{11}\text{NO}_4$ at m/z 161.07 were detected, but at relatively low intensity (rel. ints. 3–10%). It is assumed that the peak at m/z 161.07 could be formed from glucosamine by the cleavage of $-\text{OH}$ [36]. The suggested fragmentations to obtain m/z signals at 144.07 and 161.7 from glucosamine are given in Fig. 4 (these fragments were proposed previously using the electron impact ionisation source [35]). This is additional new information compared with the previous ToF-SIMS analysis for CS, where only acetylglucosamine, and not glucosamine fragments, was reported [30]. Furthermore, the degree of deacetylation was 77.6% (Table 2); therefore, mass peaks originating from acetylated chitin are also expected and, therefore, the occurrence of chitin monomers ($\text{C}_8\text{H}_{13}\text{NO}_5$) was investigated. The nominal mass of this monomer is 203 g/mol. However, the peak at m/z 203.08 had low rel. ints. (3–5%) for both CS-treated samples.

Differences were detected when comparing the spectra for the sample prepared at pH 4 (CS-R4 sample, Fig. 2) with that at pH 7 (CS-R7 sample, Fig. 3). The residual Na resulting from the pH adjustment was confirmed for the latter, as a peak of moderate intensity at m/z 22.99 was present. This signal was not detected in the CS-R4 spectrum. Peaks for the CS-R7 sample spectrum at m/z 147.90, 207.07, and 221.09 were less intense compared with the spectrum for the CS-R4 sample. This implies that the treatment at pH 4 resulted in a higher amount of CS on the viscose fibre surfaces compared with the treatment at pH 7. Additionally, for the CS-R7 sample, a peak with a rel. int. of

17% at m/z 356 was present. This peak was not detected for the CS-R4 or for the reference CV sample. The origin of that peak remains unknown.

In general, the m/z region above 400 showed more peaks in the spectrum for the CS-R7 sample than for the CS-R4 sample. This might be explained by the fact that the surface contaminants on the base viscose fibre were removed more effectively in the more acidic solution (pH 4), but retained on the fibres treated at neutral pH (similarly as for the untreated sample, as explained in Section 3.1).

Chitosan nanoparticle-treated samples (CSNP4 and CSNP7)

For both CSNP4 and CSNP7, a signal was detected at m/z 22.99, which is ascribed to the presence of Na on the surface. As this peak was present for both samples (treatment in solutions with pH 4 and 7), it most likely originates from sodium tripolyphosphate (part of the sample). The Na signal was more intense for CSNP4 compared to CSNP7.

The same as found above for CS-R4 and CS-R7, peaks at m/z 147.90, 207.07, and 221.09 were detected for both CSNP4 and CSNP7. These signals were less intense for the nanoparticles compared with the signals in the spectra for S-R4 and CS-R7; however, their presence again demonstrates that CS is attached to the surface. Part of the spectrum in the high mass region (m/z 250–900) was similar for both nanoparticle-treated samples, indicating that the surface contamination with high-molecular mass substances was similar at both pH values. In general, for both samples the positive ion ToF-SIMS spectra were similar, and no significant differences between the samples can be detected by TOF-SIMS.

Trimethyl chitosan solution-treated samples (TMC-R4 and TMC-R7)

The positive ion ToF-SIMS spectrum of TMC-R7 is given in Fig. 5. The peaks representing CS fragments were detected at m/z 58.03, 102.09, 147.90, 207.07, and 221.09. Also, the presence of the suspected contamination peaks at m/z 283 and 311 (described above) were still present.

In the ionisation procedure, a $\text{C}_3\text{H}_9\text{N}^+$ fragment (with a nominal mass of 59 g/mol) is expected to form from the TMC samples [32]. In fact, the peak at m/z 59.07 for TMC-R7 was present in Fig. 5. Compared to that peak, an even more intense peak is observed at m/z 58.03, probably originating from $\text{C}_2\text{H}_4\text{NO}^+$ [32]. The peak at m/z 102.09 in the spectrum (Fig. 5) possibly originates from $\text{C}_5\text{H}_{12}\text{NO}^+$, which could be formed from TMC, (however, to the best of our knowledge, this fragment has not been reported previously for TMC-treated samples). A signal with a rel. int. of 3% at m/z 22.99 was measured for the TMC-R7 sample, but was missing for the TMC-R4 sample. The presence of this Na signal most likely arises due to the pH adjustment with NaOH solution in the case of TMC-R7. As suggested above, the peaks at m/z 147.90, 207.07, and 221.09 represent CS, and these peaks were also detected for the TMC-R4 and TMC-R7 samples. These peaks were more intense for the TMC-R7 sample compared to the TMC-R4 sample (as shown above for the CS-treated solutions, this was the opposite of the higher intensities for CS-R7 compared to CS-R4).

In the high m/z region (above 350), peaks appeared at the same m/z , but the signals had higher intensities for TMC-R7 compared with that for TMC-R4. On the other hand, the high mass region peaks for both TMC spectra appeared at different m/z than that for the CV spectrum. Thus, the hydrocarbon contamination was different for these samples. In the TMC-treated samples, the region was dominated by the following mass fragments: a group of signals at m/z 368, 372, 382, 386, and 400, a group at m/z 495, 523, and a group at m/z 551, 661, 638, and 666.

TMC-R4 sample

TMC-R7 sample

TMCNP4 sample

TMCNP7 sample

(caption on next page)

Fig. 7. Total ion image (left images) and mapping of the mass fragments at m/z 58.03 and 102.09 on the surface of the TMC-treated samples (right images). The scale bar is 10 μm .

Fig. 8. ToF-SIMS mapping of Na at m/z 22.99 on the nanoparticle-treated samples. The scale bar is 10 μm .

Even-numbered mass fragments usually contain nitrogen. Several mass remainders were 28 mass units, possibly again referring to the cleavage of C_2H_4 from a long-chain polymer.

Trimethyl chitosan nanoparticle-treated samples (TMCNP4 and TMCNP7)

A signal for Na at m/z 22.99 was detected for both TMCNP samples. The same as explained above for the TMC solutions, peaks at m/z 58.03, and especially at m/z 102.09, were detected for these two nanoparticle samples. Moreover, the high m/z spectrum part was similar for both TMCNP samples (the same similarity as reported above for the TMC-treated solutions).

Relative amount of the adsorbed chitosan

These analyses were performed on three replicate, separately prepared, samples. The instrument used has an intensity repeatability of $\text{RSD} < 1.0\%$. The relative signal intensity ratios of the characteristic mass fragments representing the amount of CS on the surfaces are presented in Table 3. The intensity of the mass fragments at m/z 147.90, 102.09, or 58.03 originating from CS were divided by the intensity of the mass fragment at m/z 127.04, representing the hexose

monomer that originates from the cellulose viscous fibre in each sample.

The relative intensity ratio of the mass fragments at m/z 147.90 increased for all CS-treated samples compared with the CV reference (Table 3). This increment was most pronounced for the CS-R4 sample, suggesting that the highest amount of CS was adsorbed in that case (the highest among the CS and CSNP samples). In the case of the TMC and TMCNP samples, the trend in the amount of CS is $\text{TMCNP7} > \text{TMC-R7} > \text{TMC-R4} > \text{TMCNP4}$. For the latter, both mass peaks, at m/z 58.03 and 102.09, resulted in the same intensity ratio trend. The standard deviations given in Table 3 should also be taken into account, which were the highest for the TMCNP7 sample, indicating the most non-homogeneous distribution of CS on the surface. Therefore, the latter makes the CS concentration trend reported as $\text{TMCNP7} > \text{TMC-R7} > \text{TMC-R4} > \text{TMCNP4}$ less certain.

ToF-SIMS imaging

The surface distribution of CS was investigated by ToF-SIMS imaging. In the ToF-SIMS images, lighter pixels in the figure represent higher intensity – i.e. a higher intensity of signals in that spot. The signal intensity depends on the type of compound, how easily it

fragments into ions, the amount of the compound on the surface, and also the topography (secondary ions escape more easily from higher regions of the sample).

In Fig. 6, the surface topography is shown by means of the total ion image, wherein the entire mass spectrum for each pixel is included, and is employed for comparison with the fragment image. The characteristic signals for mass fragments that are indicative of CS (explained above) were mapped at m/z 147.90, 207.07, and 221.09 (Fig. 6). The signal intensities were relatively low for the CS-R7 sample, and especially for the nanoparticle-treated samples (CSNP), as clearly seen in Fig. 6. This again confirms the above statement that when comparing this set of samples, the highest amount of CS was adsorbed in the case of CS-R4 (as reported in Table 3).

Fig. 7 shows the surface distribution of TMC, which is represented by mapping the mass peaks at m/z 58.03 and 102.09 (as explained above). For the TMC-R7 sample, a particle can be seen in the total ion image, whereas this signal is missing in the fragment imaging, thus indicating that this particle was not covered with TMC.

As the presence of an Na signal (m/z 22.99) indicates the presence of nanoparticles on the surface, the distribution of Na was mapped on the nanoparticle-treated samples, both CSNP and TMCNP. These maps are shown in Fig. 8. The images were constructed from the same measurements as in Figs. 6 and 7, where the total ion distributions were shown.

Conclusions

In this work, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed to show the ability of this surface-sensitive technique to systematically study different viscose fibres treated with different solutions containing various forms of chitosan. The use of this technique provided new insights in this field of research.

Characteristic signals ascribed to viscose fibre surface contamination were explained. They most likely originate from the industrial preparation procedure. These signals were detected for all samples tested, including the untreated sample. Moreover, it was also found that these signals decreased for the viscose fibre treatment in more acidic solution with pH 4 compared to the samples prepared at neutral pH 7, the reason being that the more acidic solution removes more contaminants from the surface.

Characteristic signals for chitosan were detected at m/z 147.90, 207.07, and 221.09 originating from acetylglucosamine fragments for the samples treated in the chitosan solution. These peaks were more intense for the samples prepared at pH 4 compared with pH 7. On the other hand, fragments of glucosamine or chitin were not identified in the SIMS spectra. Some differences were also observed in the SIMS spectra for the viscose fibre treated in the chitosan solution and for the chitosan nanoparticle samples.

In the trimethyl chitosan-treated samples, the high mass region differed from the chitosan-treated samples and the untreated reference sample, which suggested that long-chain nitrogen-containing polymer was adsorbed that was different from the high-molecular mass hydrocarbon (contamination) detected on the untreated reference and in the chitosan-treated samples. Trimethyl chitosan was detected on the samples treated with a solution thereof. The characteristic peaks describing trimethyl chitosan on the surface were at m/z 58.03 and 102.09.

Finally, imaging of the sample surfaces was performed using the mass peaks at m/z 147.90, 207.07, and 221.09 for mapping the chitosan-treated samples, and the mass peaks at m/z 58.03 and 102.09 for mapping the trimethyl chitosan-treated samples. Mapping of the nanoparticles was performed at m/z 23, thus describing an Na signal that was involved in nanoparticle synthesis. This methodology enabled a clear visualisation of the different species on the solid surface and topography analysis.

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