CELLULOSE CHEMISTRY AND TECHNOLOGY

WATER RETENTION VALUE AND MECHANICAL PROPERTIES OF VISCOSE FIBRES FUNCTIONALISED BY CHITOSAN AND ITS WATER-SOLUBLE DERIVATIVE, N,N,N-TRIMETHYL CHITOSAN

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In this work, cellulose fibres coated by a chitosan solution and chitosan nanoparticles (based on chitosan and its derivative N,N,N-trimethyl chitosan),under different chemical conditions, were analysed regarding water retention value and mechanical properties, which are essential for hygiene applications. As evident from water retention value measurements, the treatment of fibres did not have a negative effect on their absorption properties, nor on their mechanical properties. Overall, the changes in tenacity and elongation did not extensively affect the properties of the final product and thus such modified cellulose fibres can be used for practical application in the field of medical textile materials.

Keywords: chitosan, N,N,N-trimethyl chitosan, water retention value, mechanical properties

INTRODUCTION

Due to the excellent properties of chitosan, such as biocompatibility, biodegradability and non-toxicity, it is a valuable material for different biomedical applications.[1-6] It has been extensively studied for wound healing, drug and gene delivery, tissue engineering, in the form of gels, membranes, sponges, scaffolds, micro- and nanoparticles, fibres and nanofibres, as well as antimicrobial coatings for textiles.[1-7] The last application is extremely interesting, requiring only the external part of the fibres(surface) to be functionalised, while antimicrobial activity should exist on the fibre interface. Among different structural forms of chitosan as a fibre coating, it has been found that chitosan nanoparticles (CSNP) have higher antimicrobial activity than the chitosan solution. It is believed that CSNP exhibit better affinity towards microbial cell wall and can be tightly bound to it due to their nano-size and higher surface area.[8-9] Thus, the trend in the application of chitosan for fibre coating lies towards its use in the form of nanoparticle dispersion.

In this work, chitosan and its water-soluble derivative, N,N,N-trimethyl chitosan, were adsorbed onto viscose cellulose fibres in the form of solution and nanoparticle dispersion.These systems were applied onto viscose fibres under different chemical conditions and then the coated fibres were further analysed regarding their water retention value (WRV)and mechanical properties. The investigation on WRV and strength properties is imperative since these properties are of great importance for in the practical use of such materials and could be affected by functionalisation treatments. Usually, medical materials require good mechanical and absorption properties. The water retention value was also compared to the zeta potential measurement, which was discussed in detail in our previous work.[10]The antimicrobial properties of the obtained chitosan coated fibres were thoroughly analysed in our previous paper, but are also briefly reported here.[10]

EXPERIMENTAL

Materials

Regenerated cellulose fibres in form of a tampon band were used as a base material for chitosan adsorption. The band was composed of two types of fibres, Lenzing Viscose® and LenzingViscostar®, mixed at a 70-30% ratio. Both viscose fibres are pure and highly absorbent, designed for manufacturing tampons, however, in LenzingViscostar®, due to its triangular cross-section, these properties are more pronounced.

The fibres were dipped into aqueous chitosan (chitosan (CS) and its water-soluble derivative, N,N,N-trimethyl chitosan (TMC)) solutions or nanoparticle dispersion (NP), which were previously prepared through ionicgelation; *i.e.* 0.1% (w/v) of sodium tripolyphosphate (TPP) solution was added to a fixed volume of chitosan or trimethyl chitosan solution in order to obtain 5:1 chitosan to TPP weight ratio. Particles were formed spontaneously under magnetic stirring for 1 h at room temperature. The final pH of CS and TMC nanoparticle dispersions (CSNP and TMCNP) was adjusted to pH=4.0 and to pH=7.0. Viscose fibres were immersed into aqueous chitosan solution or nanoparticle dispersion for 30 minutes at room temperature, using material-liquid bath ratio of 1:50, with a wet pickup of 100%.

The fibres were then squeezed on a laboratory padder (Werner Mathis AG) at the pressure of 2 bars and the speed of 2 m/min. After the excess liquid was removed, viscose fibres were dried at 40 °C for 30 min in a laboratory oven (Werner Mathis AG). Viscose fibres were then conditioned before being further analysed.

Functionalization of viscose fibres was performed using the following coatings:

1. CS or TMC solution at pH 4,
2. CSNP or TMCNP nanoparticle dispersion at pH 4,
3. CS or TMC solution at pH 7,
4. CSNP or TMCNP nanoparticle dispersion at pH 7.

Different coating procedures resulted in 8 differently treated fibre samples, which are presented in Table 1. SEM images of the fibres and the electrokinetic properties of the latter (discussed in previous work),[10] confirmed that chitosan had been introduced onto the fibre surface.

Methods

Water retention value

The water retention value (WRV) of the viscose fibres was determined according to the DIN 53 814 standard method.[11] WRV is expressed as the ratio between the mass of the retained water after 2h of soaking and 20 min centrifugation (3000 rpm), and the absolute dry mass (T = 105 °C, t = 4h) of the fibre sample.

Zeta potential

Zeta potential analysis was carried out using an Anton Paar "SurPASS" instrument, equipped with an analyzer, a data control system and a measuring cell appropriate for solid samples. An amount of 0.5 g of viscose fibres (non-treated, CS and TMC treated fibres) was placed in a cylindrical cell, while the electrolyte solution (c= 0.001 M KCl) was forced to flow through the membrane under varying pressures. Three measurements were carried out on each sample for pH values of the electrolyte solution from pH 2 to pH 10 at room temperature.

Mechanical testing

Mechanical testing of the treated and non-treated fibres was performed on an electronic dynamometer Vibrodyn 400 (Lenzing Instruments) according to the International Standard method SIST ISO 5079 – Textile Fibres: Determination of breaking force and elongation of individual fibres.[12] The influence of different chitosan treatments on the mechanical properties of fibres was determined by measuring the force and elongation using a gauge length of 10 mm, 200 mg pretention weight and a testing speed of 20 mm/min.

Table 1
Sample notations and summary of functionalization procedures of viscose fibres

Sample	Treatment of fibres
CV	Viscose fibres, untreated
CS-S4	CV treated with chitosan solution (CS) at pH 4
CSNP4	CV treated with chitosan nanoparticles' dispersion (CSNP) at pH 4
CS-S7	CV treated with chitosan solution (CS) at pH 7
CSNP7	CV treated with chitosan nanoparticles' dispersion (CSNP) at pH 7
TMC-S4	CV treated with trimethyl chitosan solution (TMC) at pH 4
TMCNP4	CV treated with trimethyl chitosan nanoparticles' dispersion (TMCNP) at pH4
TMC-S7	CV treated with trimethyl chitosan solution (TMC) at pH 7
TMCNP7	CV treated with trimethyl chitosan nanoparticles' dispersion (TMCNP) at pH 7

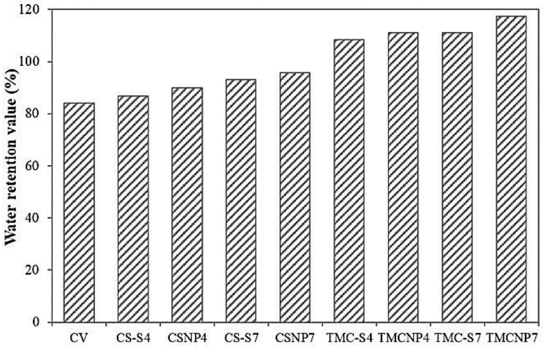

Figure 1: Water retention value of CS and TMC modified fibres

Antimicrobial testing

The antimicrobial properties of the non-treated and treated paper pulp sheets were evaluated according to ASTM E2149-01: Standard test method for determining the antimicrobial activity of antimicrobial agents under dynamic contact conditions. Gram-positive and Gram-negative bacteria, as well as fungi, were used as test organisms. The details regarding the standard technique are given in our previous article.[10]

RESULTS AND DISCUSSION

Water retention value (WRV)

In order to achieve the desired absorbency of the final product, the fibres selected need to be absorbent as well. To characterize the absorbency of cellulose fibres, water retention and water imbibition (WI) are commonly used parameters. While water retention value is a measure of the water retained in a fibre after centrifugation, water imbibition measures the water holding capacity of a loose bundle of fibres under gravitational forces.[13] It has been found out that the correlation between WI of the fibres and the tampon absorbency is extremely poor and that the correlation for the WRV is better.[13] Therefore, in this study, the water retention method has been used to characterize the hydrophilicity of functionalized fibres (Fig.1). Water retention value (WRV) determined for unmodified viscose fibres is around 84%, which is in agreement with the previously reported values in the literature.[13,14] The water retention of fibre is mainly defined by its supermolecular structure and the structure of voids, which are the driving force for water absorption in cellulose fibres.[14] Lenzing Viscose and Viscostar fibres are already designed so as to exhibit high absorption capacities. Especially Viscostar fibres enable the maximum performance on account of their star-like shaped cross-section. Chitosan is a hydrophilic, polar polymer and should, after being bonded onto fibres, increase the hydrophilicity of the coated fibres and consequently their water absorption capacity. However, it is supposed that the conformation of the chitosan attached onto the fibre surface may also influence the fibre's accessibility for water. When chitosan is bound onto fibres as an extended polymer chain (at pH 4), the packing density of fibres may increase and thus the sorption capacity could be lowered. When chitosan is adsorbed onto fibres from a coiled structure (at pH 7) or in the form of nanoparticles, the fibres do not adhere to each other as tightly and thus the sorption capacity should not be inhibited intensively.

In Figure 1, it can be seen that water absorption capacity increases with an increasing amount of chitosan adsorbed on the fibresurface. The samples, such as CSNP7 and TMCNP7, which exhibited the highest quantity of chitosan, determined previously with XPS and zeta potential analysis,[10] show the highest WRV. Among CS treated fibres, CSNP7, which had the highest % of N,[10] demonstrate a greater potential for water retention than other samples. The increase in WRV for sample CSNP7 is more than 10% higher compared to untreated CV fibres. If the treatment with chitosan nanoparticles is compared with the treatment with the chitosan solution, a slight increment in WRV is observed for sample CSNP4, compared to CS-S4, and the same for CSNP7 compared to CS-S7, indicating that chitosan nanoparticles create a more hydrophilic surface due to their nano-size, and consequently induce higher swelling of the fibres. With the introduction of TMCon the fibre surface, the ability of the fibres to retain water is even greater. The increment in WRV, compared to pure CV, is between 24% and 33%, depending on the treatment process used for applying TMC on the fibres. The WRV determined for TMCNP7 sample was 117%, which is the highest WRV of all fibres tested, and is almost 9% greater than for sample TMC-S4 and 6% greater when related to TMCNP4 and TMC-S7. Improved water retention ability was noted for the samples treated with TMC nanoparticles (TMCNP4, TMCNP7), compared to the samples treated with pure TMC solution (TMC-S4, TMC-S7). The same effect was observed for CS and CSNP coated samples and, as has been pointed out above, the reasons lie in the particle nanostructure, as well as in the more open structure (less compact structure of coating) of the fibres when coated by the nanoparticle dispersion.

The fibres with adsorbed TMC have a higher WRV, compared to the fibres functionalized with CS, because TMC polymer has more positively charged functional groups at pH 7 as shown in our previous paper,[10] which contribute to the higher hydrophilicity and better adsorption capacities.

One of the alternative methods used to characterize the hydrophilicity of fibre surface is to determine the electrokinetic properties of the fibres.[10] Since adsorption of water causes an interfibrillar swelling in the fibres, the size of an active surface increases, causing a shift of the shear plane into the liquid, which leads to a reduction of ZP.[10] The WRV of viscose fibres functionalized with CS and TMC can thus be correlated with the swelling of the fibres and the subsequent reduction of the absolute values of negative ZP. A detailed discussion regarding the ZP results of the fibres modified with both chitosan formulations has been provided earlier.[10] This study points out the correlation between ZP plateau values in the alkaline region of the fibres as a swelling indicator and WRV.

More pronounced swelling was observed for the TMC treated fibres, compared to the CS treated fibres, independently of the pH and of the chitosan structure adsorbed, as endorsed with WRV measurements. Figure 2 presents the correlation between ZP plateau values in the alkaline region of the fibres and WRV. The higher the absolute value of ZP (as indicator of more swollen fibres) is, the higher the WRV. The correlation between both methods is almost linear, indicating the relevance of the results obtained for the fibre sorption capacities.

Mechanical properties of fibres

Breaking force and elongation of fibres are very important parameters, which need to be considered in designing fibres with added value in order to tailor their performance according to the desired end properties. Any chemical or physical modification can alter the mechanical properties of fibres. Therefore, it is essential to estimate the influence of the coating procedures used on the mechanical properties of the fibres. The results of breaking force for unmodified and modified fibres are presented in Figure 3. The force necessary to break unmodified viscose fibres was 6.45 cN. However, modifying fibres with CS and TMC has affected the breaking strength. The most noticeable change was observed after the treatment with the CS solution at pH 4, where breaking strength was reduced by 7%. Coating fibres with chitosan nanoparticle dispersions at pH 4 (CSNP4) and pH 7 (CSNP7) reduced the force needed to break the fibre by about 2%, while coating with CS solution at pH 7 (CS-S7) caused a 2% increase. The fibres treated with the TMC solution at pH 4 (TMC-S4) and the TMC nanoparticle dispersion at pH 4 (CSNP4) also caused an increase, *i.e.* by 3% and 4.8%, respectively.

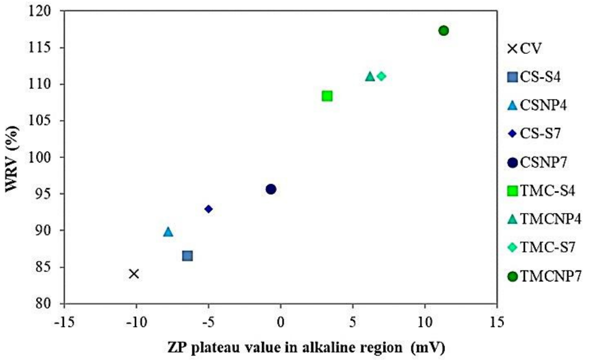

Figure 2: Correlation between zeta potential and water retention of coated cellulose fibres

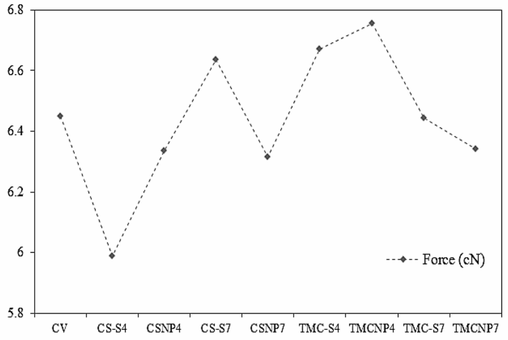

Figure 3: Breaking force of CS and TMC modified fibres; coefficient of variation – lower than 2% for all samples

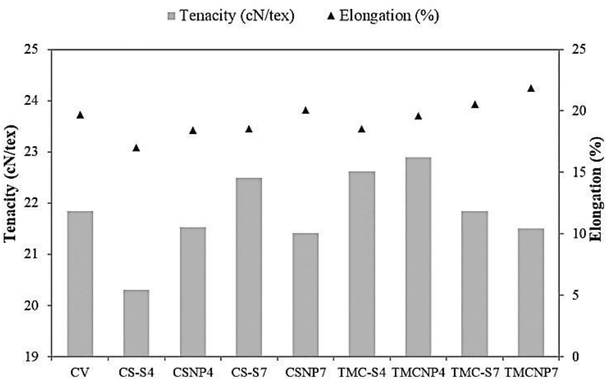

Figure 4: Tenacity and elongation of CS and TMC modified fibres

The modification of fibres performed with the TMC solution at pH 7 (TMC-S7) did not affect the force, but coating with the TMC nanoparticle dispersion at pH 7 (TMCNP7) did cause a 2% decrease in force, which does not alter sorption properties to such an extent. In this way, chitosan nanoparticles may be used instead of chitosan macromolecules (acidic chitosan solution that may worsen mechanical properties). Thus, the attachment of chitosan in the nanoparticle form can be targeted in some places only, avoiding full covering of the fibre surfaces or filling their internal part.

The results for tenacity and elongation of fibres before and after the treatment with CS and TMC are presented in Figure 4. Tenacity is defined as the value of specific stress at a fibre's break and is calculated from the force, divided by the linear density of fibres. Thus, the results for tenacity show a similar trend as those determined for the force. The tenacity of viscose fibres before the treatment was around 22 cN/tex. After the treatment with CS and TMC, slight changes in tenacities were observed. The most pronounced change was noticed for sample CS-S4, as already seen from the force measurements (Fig. 4). Compared to untreated CV fibres, the decrease of tenacity for CS-S4 is approximately 1.5 cN/tex, which is less than the standard deviation determined for all the tenacity measurements. Sample CS-S4 also exhibited the lowest elongation (17%). The elongation of untreated CV fibres was around 20%. An increase by 1 cN/tex in tenacity was observed for the sample treated with TMC nanoparticle dispersion at pH 4 (TMCNP4). This was the highest value of tenacity (23 cN/tex) determined, whereas the highest elongation was obtained for TMCNP7 sample (22%), *i.e.* the sample treated with TMC colloidal dispersion at pH 7. The treatment of fibres with CS colloidal dispersion at pH 4 (CSNP4) had a lower influence on elongation than the treatment with the bulk CS solution at the same pH (CS-S4); comparable values of elongation of the CS-treated fibres at pH 7 were also observed. TMC seemed to have a similar impact on the elongation of the fibres as CS.

It has to be pointed out that all values are in a narrow range and standard deviation could be of the same order with the differences between the samples, thus the differences are negligible and due to chance.

The results presented above demonstrate that by introducing CS and TMC onto fibres leads to negligible deterioration of mechanical properties, because chitosan's interactions are obviously restricted to the cellulose fibre surface without affecting the molecular and supramolecular and/or fibrillary structure of the cellulose polymer.

Brief report on antimicrobial testing

The antimicrobial activity of fibres functionalised by CS and TMC with different structural forms (Table 1) is discussed in detail in our previous article.[10] If summarized, it has been shown that the CS-coated materials exhibit higher overall inhibition of microorganisms than the TMC-coated materials, independently of the treatment pH. It has been shown that all fibres treated with TMC are ineffective against *E. coli*. They also show reduced activity against *C. albicans* fungi, meanwhile the fibres functionalized by CSNP (CSNP4 and CSNP7) are the optimal option regarding antimicrobial efficiency; they assure antimicrobial activity against microorganisms such as S. *aureus*, *E. coli* and *C. albicans*. These pathogens quite often cause problems on skin or mucosa (mouth, vaginal), as well as in wounds, and thus functional fibres with antimicrobial activity are of great importance in the field of medical care.

As has been shown in previous work, chitosan has a great potential as coating for medical materials.[15] It must be pointed out that the functionalization process is technologically and economically suitable to be transferred to real life conditions, while some environmental aspects must be still studied and fulfilled.[16]

CONCLUSION

The sorption capacity and mechanical properties of fibres functionalised by chitosan in different structural forms were tested. As evident from the WRV measurements, the treatment of fibres did not have a negative effect on their absorption properties, nor on their mechanical properties. Overall, the changes in tenacity and elongation did not affect the end properties of the final product to a great extent. The results clearly suggest the potential applicability of all mentioned functionalization procedures for manufacturing *e.g.* sanitary textiles, such as hospital sheets, antimicrobial patches, *etc.* Viscose fibres functionalised by CSNP are especially well suited for the latter, as they achieved superior antimicrobial properties and are ideal for medical use, where quite often good absorption ability and mechanical properties are required as well.

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