MATERIALS CHEMISTRY | RESEARCH ARTICLE

Environmentally benign chitosan-based nanofibres for potential use in water treatment

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Abstract: Chitosan (CS)-based nanocomposite materials are highly prone to swelling when in contact with water. It is therefore essential to modify them to enhance their resistance to swelling, in order to be applicable in water treatment. In this study, the CS-based nanofibres were prepared using the electrospinning technique. The nanofibres were prepared from a polymer blend of CS, and other polymers (polyacrylamide (PAA) and polyethylene glycol (PEG)) added in small optimized quantities to enhance the ability to electrosprun CS. Elastic polyisoprene (PIP) and functionalized multi-walled carbon nanotubes (f-MWCNTs) were incorporated in the electrospinnable solution blend of CS, PAA and PEG to reduce the swelling behaviour of the CS-based nanofibres and to improve their mechanical strength and thermal properties. PIP did not only improve the morphology of the resulting nanofibres but also reduced their swelling behaviour by twofold. The addition of f-MWCNTs was found to improve the tensile strength of the nanofibres by twofold, relative to nanofibres with no f-MWCNTs. The thermal degradation of the nanofibres was improved by a magnitude of 50°C. Antibacterial silver (Ag) and iron (Fe) nanoparticles (NPs) were embedded on the nanofibres for their possible use in disinfection processes.

ABOUT THE AUTHORS
This work was conducted by a master's student working in the research group of Professor Sabelo Mhlanga at the University of South Africa. The research group led by Prof Mhlanga largely involves finding sustainable solutions (materials) to solve problems relating to water quality within the context of the water-energy-food nexus. The approach involves applying the principles of green chemistry, nanoscience and nanotechnology to develop materials for drinking and wastewater treatment. In particular, there is keen interest in developing energy efficient technologies for drinking water treatment in rural communities, and we recently completed a flagship project supported by the National Research Foundation (South Africa). The flagship project entailed synthesis of various nano-structured materials (such as thin films, nanofibres and nanobeads) with the desired size (nanometre dimensions) and enhanced physicochemical properties. “Green” chemical synthesis approaches were applied through careful selection of reaction conditions, e.g. appropriate choice of precursors, solvents and energy requirements.

PUBLIC INTEREST STATEMENT
This research paper presents an alternative way to produce stable chitosan-based polymers that can be used in water purification. Chitosan-based polymers were made into small threads (fibres) with nanoscale sizes using an electrospinning technique under optimized conditions. The major objective of the research was to control the swelling capacity of the chitosan-based nanofibres when in contact with water and to improve its mechanical properties. This was achieved by blending chitosan with small amounts of other polymers such as polyisoprene and functionalized multi-walled carbon nanotubes. The result was that the nanofibres had reduced swelling capacity when in contact with water and to improve its mechanical properties. This was achieved by blending chitosan with small amounts of other polymers such as polyisoprene and functionalized multi-walled carbon nanotubes. The result was that the nanofibres had reduced swelling capacity when in contact with water and to improve its mechanical properties. This was achieved by blending chitosan with small amounts of other polymers such as polyisoprene and functionalized multi-walled carbon nanotubes. The result was that the nanofibres had reduced swelling capacity when in contact with water and to improve its mechanical properties. This was achieved by blending chitosan with small amounts of other polymers such as polyisoprene and functionalized multi-walled carbon nanotubes.
These NPs have demonstrated a potential to kill bacteria in water and, therefore, the prepared nanofibres can be used in disinfection water treatment processes with reduced swelling capacity.

Subjects: Bioscience; Physical Sciences; Engineering & Technology

Keywords: chitosan; electrospinning; multi-walled carbon nanotubes; swelling; polyisoprene

1. Introduction

Chitosan (CS) is a copolymer of β-(1-4)-2-deoxy-2-amino-D-glucopyranose and β-(1-4)-2-deoxy-2-acetamino-D-glucopyranose units (1, 2). It is a non-toxic, biodegradable and biocompatible polycationic polymer. CS is obtained from the partial deacetylation of chitin using specific concentration of sodium hydroxide at a certain hydrolysis time and temperature, depending on the desired degree of deacetylation (3). CS is the most abundant biopolymer, second to cellulose acetate due to the high availability of chitin obtained from crab, shrimp shells, insects, crustaceans, annelids, molluscs, coelenterata and fungal mycelia (4).

Nanofibrous composite materials such as CS nanofibres have received a considerable attention due to their remarkable properties and abundant availability of CS. They are easily modified with specific functional groups for the uptake of certain pollutants (5, 6, 7, 8). Their size and structural morphology can be controlled during synthesis (9). CS has been reported to have good binding interactions with nanomaterials such as carbon nanotubes (CNTs), silver (Ag), iron (Fe) and gold (Au) nanoparticles (NPs), thus preventing agglomeration and providing uniform dispersion of these nanomaterials (10–13).

CNTs are cylindrical nano-structured allotropes of carbon. Due to their unique thermal and mechanical properties, CNTs are used as additives in many applications (14) including remediation in contaminated water sources (15). On the other hand, Ag and Fe NPs supported on different polymers have gained considerable interest/attention in the microbiology due to their strong biocidal properties (5, 16, 17). As such, nanocomposites prepared from polymers and NPs have shown effective contribution to a range of applications, which include scaffolding in bone tissue engineering, wound dressing and water treatment (18, 19).

Nanofibrous materials are polymeric non-woven nano-structured materials comprising of one component with at least one dimension less than 100 nm. These materials are fabricated using different strategic methods such as graft polymerization, in-situ polymerization and solution blending (19, 20). The most prominent techniques employed in the fabrication of nanofibres are, but not limited to air-blast atomization of mesophase pitch, pulling of non-polymer molecules by an atomic force microscope (AFM) tip, laser-assisted catalytic growth, electrospinning (21, 22). For efficient application, researchers have synthesized these materials in tubular forms, as hollow fibres, as well as porous structures. The major challenge has been the inability to produce materials with desired nanoscale sizes (23). However, using the electrospinning technique, the ability to produce nanofibres with diameters in the nanometre scale has become possible (24).

CS exhibits physical, chemical and biological properties that can be modified to render this material applicable in water treatment. The presence of amino and hydroxyl groups on CS helps in metal chelation (25, 26) and interacting with the thiol groups on the bacterial cell wall and cell membranes, thereby affecting the respiratory system of the bacteria (27, 28). However, its application in water treatment still requires further exploration since it has some limitations such as swelling and low mechanical strength (29). In this work, small quantities of multi-walled carbon nanotubes (MWCNTs) and polyisoprene (PIP) were blended with CS to improve the mechanical properties, thermal stability and to reduce the swelling behaviour of the CS-based nanofibres.
2. Experimental

2.1. Materials
Chitosan (MW = 150,000 g mol⁻¹, 75 degree of deacetylation), polyisoprene (MW; 35,000 g mol⁻¹), polyacrylamide (MW = 700,000 g mol⁻¹), polyethylene glycol (MW = 6,600 g mol⁻¹), glutaraldehyde (25% w/v), iron chloride hexahydrate, glacial acetic acid (99.9% w/v), sulphuric acid (98.0% w/v), nitric acid (70% w/v) were supplied by Sigma-Aldrich (Germany). Silver nitrate was purchased from Rochelle Chemicals (South Africa). Deionized water was prepared in the laboratory using direct-Q® (Millipore) system supplied by Merck Millipore (South Africa). All reagents were used as received.

2.2. Hydrolysis of chitosan
CS was hydrolysed to improve the degree of deacetylation. Approximately 5 g of CS was added to 50% NaOH (30 mL) in a round-bottom flask equipped with a condenser. The contents of the flask were refluxed at 80°C for 48 h and then filtered after cooling. The hydrolysed CS was washed with the aliquots of acetone, three times and dried in an oven at 60°C for 12 h.

2.3. Synthesis and purification of MWCNTs
MWCNTs with average diameter of 30 nm were synthesized following the procedure reported by Mhlanga et al. (30). The MWCNTs were purified using a mixture of H₂SO₄ and HNO₃. This involved transferring 0.2 g of the as-synthesized MWCNTs into a 25-mL solution of sulphuric acid/nitric acid mixture (3:1) in a 100-mL round-bottom flask equipped with a condenser. The contents of the flask were refluxed at 120°C for 24 h. The resulting mixture was diluted with 1,000 mL of de-ionized water and filtered. The rinsing was repeated until the filtrate was at neutral pH. The oxidized MWCNTs (f-MWCNTs) were dried in an oven at 60°C for 48 h.

2.4. Preparation of electrospinning solutions

2.4.1. Chitosan solution
The concentration of CS was varied to find the critical viscosity/concentration needed for electrospinning solution of CS. CS powder was transferred to a clean beaker and dried in the oven at 70°C for 24 h and cooled in a desiccator. CS solutions (2.0, 2.5, 3.0 and 3.5%) were prepared by weighing 0.2, 0.25, 0.30 and 0.35 g of CS and transferred into four 50-mL round-bottom flasks fitted with a condenser. Glacial acetic acid (10 mL, 50%) solution was added into each flask containing CS powder. The contents of the flasks were heated to 50°C and stirred for 24 h and then centrifuged for 3 min at 78,000 rpm to remove the suspended particles. The resulting CS solutions were transferred into the clean glass bottles and were ready for electrospinning.

2.4.2. Blending of CS to enhance its functionality
Different polymers were blended with CS to enhance its ability to be electrospun. Polyacrylamide (PAA) was added to the CS at these ratios: CS:PAA = 70:30, 78:22 and 80:20. PEG (5%) was also added to the blends of the above polymers to reduce the surface tension of the resulting solution. Subsequently, PIP was added to the solutions (PAA:CS:PEG) to improve the morphology and reduce the swelling behaviour of the nanofibres. The PIP amounts added were 20, 40, 60, 80 and 100% relative to CS. The resulting solutions were transferred into the glass bottles and were ready for electrospinning.

To prepare nanofibres with 2 wt% f-MWCNTs, 4 mg of the f-MWCNTs was added to 0.2 g of total mass of CS–PAA–PEG–PIP in a round-bottom flask containing glacial acetic acid (50%). The contents of the flask were stirred at 50°C for 24 h to achieve a homogeneous mixture. The resulting solutions were ready for electrospinning.
To prepare the polymer solution containing 2 wt% of Ag and Ag/Fe NPs, the previously reported method was followed \(^{(5)}\). Precisely calculated masses of silver nitrate (0.0064 g) and iron(III) chloride (0.012 g) were mixed with 0.2 g of total mass of CS–PAA–PEG–PIP in a round bottom flask as reported. The contents of the flask were stirred at 50°C for 24 h to achieve a homogeneous mixture. The resulting solutions were ready for electrospinning.

### 2.5. Electrospinning of the polymer solutions

In order to prepare CS-based nanofibres, the prepared solutions from Section 2.4 were transferred to a 10-mL plastic syringe fitted with a needle of 0.8 mm internal diameter. The syringe was placed on a NE-4000 double-syringe pump. A high-voltage generator was used to induce an electric field between the collecting plate and the tip of the needle. The positive terminal of the direct current (DC) generator was connected to the tip of the syringe needle and the negative terminal connected to the aluminium foil (collecting plate). The nanofibres were synthesized at the following optimized electrospinning conditions: syringe injection flow rate of 0.3 mL·h\(^{-1}\), a distance of 9 cm between the aluminium foil and the tip of the needle and a voltage of 14 kV at room temperature.

### 2.6. Cross-linking of nanofibres

The electrospun nanofibres were dried in an oven at 40°C for 24 h to remove moisture and then placed and supported at the top of the beaker which was saturated with the vapour of 25% glutaraldehyde (GLA) for 24 h. The resulting cross-linked nanofibres were dried in an oven for 24 h. The schematic representation for cross-linking of the CS-based nanofibres using GLA is shown in Figure 1.

### 2.7. Characterization of CS-based nanofibres

The CS-based nanofibres were characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared (FTIR) spectrophotometer, Raman spectrophotometer, thermogravimetric analyser (TGA), X-ray diffractometer (XRD), tensile tester and water absorption. From these characterizations, the morphology, dispersion of nanoparticles on the nanofibres, polymerization, functionality, thermal degradation, mechanical strength and the swelling behaviour the nanofibres were ascertained.

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**Figure 1.** Schematic representation for the cross-linking of CS-based nanofibres.
3. Results and discussion

3.1. Elemental analysis

The degree of deacetylation of as supplied and hydrolysed CS was calculated using the elemental results shown in Table 1 and Equation (1). The results were reported as % C, H and N for the purpose of degree of deacetylation calculations. The calculated degree of deacetylation of as supplied CS presented in Table 1 was found to be 74.9%, which was similar to that reported by Sigma-Aldrich (75%). Hydrolysing CS with 50% NaOH for 48 h was found to increase the degree of deacetylation to 82.7%. It has been shown that hydrolysis of CS results in cleavage of acetamide bonds which leads to deacetylation rather than the oxidative degradation of the glycoside bonds (31).

\[
DD = \left(1 - \left(\frac{C}{N} - 5.145 \times \frac{6.816 - 5.145}{100}\right)\right) \times 100\%
\]

where DD is the degree of deacetylation; C is the carbon content in percentages; N is the nitrogen content in percentages.

3.2. Scanning electron microscopy analysis

3.2.1. Optimization of polymer concentration

The concentration of the CS powder was varied to determine the critical viscosity/concentration which is easy to electrospin. When 2 and 3% of CS (75% DD) and 3% concentration of hydrolysed CS were electrospun, the solution formed a droplet at the tip of the needle which immediately formed a cone that was followed by a jet towards the surface of the aluminium foil (Figure 2(a–c)). The SEM images showed no formation of nanofibres at these concentrations. This was attributed to the low concentration of the

<table>
<thead>
<tr>
<th>Table 1. The elemental composition of as supplied and hydrolysed chitosan</th>
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<tr>
<td>Element</td>
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<tr>
<td>-------------------</td>
</tr>
<tr>
<td>As supplied CS</td>
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<tr>
<td>Hydrolysed CS</td>
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Figure 2. SEM images of electrospun CS polymers: (a) 2.5% CS, (b) 3.0% CS, (c) 3% hydrolysed CS, (d) 3% hydrolysed CS/PAA blend at a ratio of 60:40, (e) 3% hydrolysed CS/PAA blend at a ratio of 60:40 and 5% PEG relative to CS.
CS solution which was not sufficient to stabilize the charged jet, hence breaking the jet into smaller droplets (a process called electrospraying) (32). When the concentration of the CS was increased to 3.5%, the solution became too viscous such that it could not be released out of the syringe.

In an attempt to overcome the challenges and difficulties associated with electrospinning of CS, the CS was blended with PAA with the aim of maintaining CS at a higher amount relative to PAA since CS was the polymer of interest. When hydrolysed CS was blended with PAA at a ratio of 60:40 (maintaining the polymer solution at 3%); the short broken nanofibres were collected at the aluminium foil (Figure 2(d)). PAA is a high molecular weight polymer that is known to form hydrogen bond with other polymers and assists in the stabilization of the charged jet of the solution under an electric field (33). Figure 2(e) shows long CS nanofibres formed in layers when 5% of PEG relative to CS was added to the 60:40 blend of hydrolysed CS and PAA. PEG helped to reduce the surface tension of the viscous CS polymer and consequently improve its ability to be electrospun (34).

3.2.2. Effect of ratio of blended polymers

The ratio of CS:PAA was varied to monitor the effect of PAA on the morphology of the CS nanofibres. PEG (5%) relative to CS (by weight) was added to all blends of CS:PAA in order to reduce the surface tension of the viscous CS solutions. Non-beaded nanofibres were obtained at a CS:PAA percentage ratio of 70:30 and 78:22 with no electrospraying (Figure 3(a) and (b)). When CS:PAA was electrospun with the polymer ratio of 80:20, the nanofibres were accompanied by the formation of small fine solution droplets (Figure 3(c)). This indicated that electrospinning was accompanied by electrospraying at this polymer ratio. This was explained by the inability of the stretched polymer to sustain stream break-up when the electric field is applied to the polymer solution. At this polymer ratio, the amount of PAA was believed to be at a lower characteristic concentration needed to stabilize the polymer jet that can be drawn into small and fine non-woven fabrics. Since CS was the main polymer of interest, the CS/PAA blend that produced nanofibres with better morphology at the highest amount of CS in the blend, i.e. (CS:PAA ratio of 78:22) was used for further blending with PIP which was intended to reduce the swelling behaviour of the CS-based nanofibres (Table 2).

<table>
<thead>
<tr>
<th>Electrospinning Solutions</th>
<th>Ratio</th>
<th>wt%</th>
<th>Conductivity (10^3 Sm/cm)</th>
<th>Specific viscosity (ηsp)</th>
<th>Fibre morphology</th>
</tr>
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<tbody>
<tr>
<td>CS</td>
<td>-</td>
<td>2.5</td>
<td>3.6</td>
<td>2.3</td>
<td>No nanofibres</td>
</tr>
<tr>
<td>CS</td>
<td>-</td>
<td>3</td>
<td>4.2</td>
<td>3.7</td>
<td>No nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS</td>
<td>-</td>
<td>3</td>
<td>4.6</td>
<td>3.4</td>
<td>No nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS + PAA</td>
<td>60:40</td>
<td>3</td>
<td>2.3</td>
<td>1.8</td>
<td>Non-uniform nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS + PAA + 5% PEG</td>
<td>60:40</td>
<td>3</td>
<td>2.6</td>
<td>1.6</td>
<td>Beaded nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS + PAA + 5% PEG</td>
<td>70:30</td>
<td>3</td>
<td>2.6</td>
<td>1.7</td>
<td>Uniform nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS + PAA + 5% PEG</td>
<td>78:22</td>
<td>3</td>
<td>2.7</td>
<td>1.9</td>
<td>Uniform nanofibres</td>
</tr>
<tr>
<td>Hydrolysed CS + PAA + 5% PEG</td>
<td>80:20</td>
<td>3</td>
<td>2.9</td>
<td>2.3</td>
<td>Electrospraying on nanofibres</td>
</tr>
</tbody>
</table>
3.2.3. Addition of PIP into CS/PAA/PEG polymer blends

Different amounts of PIP were added to the CS/PAA/PEG (ratio of 78:22 and 5% PEG relative to CS) blend that gave the uniform nanofibres with homogeneous appearance under SEM analysis. The addition of 20–40% PIP relative to CS did not significantly change the morphology of the CS nanofibres (when comparing with the CS nanofibres presented in Figures 3(b) and 4(a) and (b). A further increase in PIP added (i.e. 60–80%) resulted in homogeneous nanowebs with improved morphology (Figure 4(c) and (d)). When the concentration of PIP was increased to 100% (i.e. PIP and CS at the ratio of 1:1), the homogeneity of the entangled nano-structured webs was lost and the nanofibres became beaded (Figure 4(e)).

All these changes in morphology of the nanofibres were attributed to the concentration of elastic PIP, which enabled the CS solutions to stabilize the bending of the jet in the electric field between the tip of the spinneret and the collecting plate. PIP may have affected different parameters such as viscosity, surface tension and conductivity of the solution that affected the electrospinning either positively or negatively. The surface tension helps to sustain the whipping and stretching of the polymer solution (35, 36), whilst the viscoelastic PIP maintains the stream break-up of the jet (37). These two parameters are affected by the polymer concentration which encourages the development of entanglement to produce smooth and uniform nanofibres at characteristics electrospinning polymer concentration (38).

The uniform non-beaded nanofibres were obtained with the 3% blended polymers with the following ratios: CS:PA at 78:22, 5% PEG and 80% PIP relative to CS. The remaining challenge was to synthesize the nanofibres with nanoscale sizes to improve their application as high surface area materials in the removal of pollutants from water. In this case, the blended CS/PAA/PEG/PIP solutions that produced uniform nano-structured non-woven fabric material with improved morphology were used for optimization of electrospinning parameters such as flow rate, distance between the tip of the needle and voltage, to determine the parameters that produced CS-based nanofibres with smaller diameters.
3.2.4. Cross-linked CS-blended nanofibres

Figure 5 shows the SEM images of non-cross-linked and cross-linked CS-based nanofibres containing Ag and Fe NPs and f-MWCNTs. It is known that addition of salts affects the charge carrying capacity of the polymer during electrospinning (39). The alteration of charge density may affect the formation of Taylor cone if the charge carrier concentration is higher than the maximum threshold (39, 40). The SEM images showed that addition of Ag⁺, Fe³⁺ ions and MWCNTs to the optimized concentration of blended CS solution did not have a significant effect on the integrity of the nanofibres. This was associated to the concentration of the charge carriers (Ag⁺ and Fe³⁺) added in the optimized concentration of the polymers.

It is therefore believed that addition of Ag⁺ and Fe³⁺ ions did not increase the charge density of the electrospinning solution of blended CS beyond the maximum threshold, hence no alteration to the integrity of the nanofibres. Both cross-linked and non-cross-linked nanofibres were characterized by uniform non-woven nanofibre mats. The integrity of the nanofibres was maintained after cross-linking with GLA. There was no structural deformation observed. However, the size of the cross-linked nanofibres increased from 471 ± 139 nm (Figure 5(a)) to 627 ± 284 nm (Figure 5(b)). This was ascribed to the swelling behaviour of the CS-based nanofibres due to absorption of the moisture during cross-linking.

3.3. TEM analysis

TEM images indicated the successful embedment of the Ag and Ag/Fe NPs of the surface of the nanofibres (Figure 6). The NPs were observed to grow on the surface of the nanofibres after photochemical reduction of the respective metal ions of these NPs. In the previous studies, it was indicated that the growth of the NPs depends on the time of irradiation of the nanofibres these metal ions (5, 18). It is believed that during photochemical reduction, the migration of the Ag⁺ and Fe³⁺ ions is activated to the surface on the nanofibres, which leads to the aggregation of these ions to be reduced, while on the surface of the nanofibres. The Ag NPs were agglomerated on the surface of the nanofibres compared to the well-distributed Ag/Fe NPs. This indicated that, the presence of the Fe NPs assisted in the distribution of the Ag NPs due to their high electrical conductivity nature. The XRD, UV-Vis and EDS-coupled TEM results have also indicated the presence of Ag and Fe NPs on the surface of the nanofibres and such results are available in these citations (5, 18).

3.4. Fourier transform infrared spectroscopy analysis

3.4.1. Oxidation and purification of multi-walled carbon nanotubes

The FTIR analysis of f-MWCNTs was done to ascertain the presence of the functional groups on the surface. The characteristic vibrational frequencies of the MWCNTs were recorded at 200–4,000 cm⁻¹. The FTIR spectra of as supplied and f-MWCNTs are shown in Figure 7. The peaks at 1,617 and
1,056 cm\(^{-1}\) were due to stretching of C = C and C–O, respectively. The peaks at 621 and 3,237 cm\(^{-1}\) were due to vibrations of C–C and bending of C–H. The peaks at 3,415, 3,476 and 3,551 cm\(^{-1}\) were due to vibrations, bending and stretching of O–H (Figure 7(a)). The FTIR spectra of oxidized MWCNTs showed a shift of the C = C and C–O stretches to 1,618 and 1,030 cm\(^{-1}\), shift of C–C and C–H vibrations to 612 and 2,924 cm\(^{-1}\) and O–H stretch to 3,413 cm\(^{-1}\) (Figure 7(b)).

These shifts were associated with the strains induced during rearrangement of atoms when catalysts are removed, the internal ordering and local chemistry at the surface of the f-MWCNTs (41, 42). The carboxylation of MWCNTs was confirmed by the appearance of the carbonyl group at 1,731 cm\(^{-1}\) and the intensified C–O peak at 1,030 cm\(^{-1}\) (Figure 7(a)).

### 3.4.2. Hydrolysed chitosan

The characteristic vibrational frequencies that correspond to as-supplied and hydrolysed CS were recorded at 200–4,000 cm\(^{-1}\). The transmitted peaks at 2,871, 1,201, 1,652, 1,024 and 894 cm\(^{-1}\), 668 cm\(^{-1}\) are characteristic vibration frequencies of C–H, C–O, C = O, C–N, saccharine structure of CS and C–C, respectively (Figure 8(a) and (b)). The broad peaks at 3,301, 3,305 cm\(^{-1}\) were assigned to vibrational stretches of O–H and N–H. Peaks of hydrolysed CS showed a shift of C–H, C–O, C–N, C–C to 2,882, 1,251, 662 cm\(^{-1}\), respectively. The disappearance of the acetyl absorption peak of deacetylated CS at 1652 cm\(^{-1}\) showed improved degree of deacetylation of CS (Figure 8(b)).
3.4.3. Chitosan blended with PAA/PEG/f-MWCNTs and cross-linked with glutaraldehyde

The FTIR analysis of nanofibres prepared from the solution of blended polymers was also conducted. The characteristic vibrational frequencies that correspond to the nanofibres prepared from CS, CS blended with PAA/PEG/PIP/f-MWCNTs and the cross-linked nanofibres were recorded at 200–4,000 cm⁻¹. The FTIR spectra of aforementioned nanofibres are shown in Figure 9. The peaks at 3,326 and 2,882, 1,251, 1,040, 662 cm⁻¹ were due to stretching of O–H and N–H, bending of C–H, stretching of C–O, C–H bending and vibrations of C–C (Figure 9(a)).
The peaks at 3,324, 2,883, 1,533, 1,259, 1,017, 707 cm\textsuperscript{-1} on Figure 9(b) are due to O–H and N–H stretching, C–H bending, C–O stretching, C–N stretching, C–C vibration which thus showed the presence of all functional groups of polymers blended. The peaks at 2,939, 1,714, 1,569, 1,240, 1,012, 671 cm\textsuperscript{-1} on Figure 9(c) were due to C–H bending, C=N stretching, C=O stretching, C–O stretching, C–N stretching, C–C vibrations. The peak that appeared at 1,714 cm\textsuperscript{-1} due to C=N indicated the successful cross-linking of the CS as a result of nucleophilic substitution of the electron-rich amines groups from CS and the electron-deficient carbon on GLA (Figure 9(c)).

3.5. Raman spectroscopy analysis of CS nanofibres blended with PAA/PEG/PIP/f-MWCNTs

Figure 10 presents the Raman spectra of as-synthesized MWCNTs, f-MWCNTs and CS/PAA/PEG/PIP/f-MWCNTs blends. The graphite (G) and disorder (D bands were observed at the following wave numbers 1,596 and 1,298 cm\textsuperscript{-1} for as-synthesized MWCNTs (Figure 10(a)), 1,598 and 1,301 cm\textsuperscript{-1} for f-MWCNTs (Figure 10(b)) and 1,521 and 1,305 cm\textsuperscript{-1} for nanofibres prepared from CS/PAA/PEG/PIP/f-MWCNTs blends (Figure 10(c)). The D bands observed were due to several factors which include grain boundaries and size defects which affected the crystallinity of the MWCNTs (43).

To measure the effect of oxidation on the defects of the MWCNTs, the ratio of the intensity of the D and G bands (I\textsubscript{D}/I\textsubscript{G}) was determined and compared. Table 3 presents the ratio of the intensities of the D and G bands. The ratio of I\textsubscript{D}/I\textsubscript{G} of as-supplied MWCNTs, f-MWCNTs and nanofibres prepared from CS/PAA/PEG/PIP/f-MWCNTs nanofibre blends were found to be 1.67, 1.25 and 5.10, respectively. The ratio of I\textsubscript{D}/I\textsubscript{G} was found to decrease when the as-supplied MWCNTs were oxidized using the HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} mixed acid system. The decreased I\textsubscript{D}/I\textsubscript{G} ratio showed the increased graphite-induced band relative to disorder induced band, hence increased purity of the f-MWCNTs. The I\textsubscript{D}/I\textsubscript{G} ratio of the nanofibres prepared from CS/PAA/PEG/PIP/f-MWCNT blend was high, indicating the increased

![Figure 10. Raman spectra of CS-based nanofibres: (a) as-synthesized MWCNTs, (b) f-MWCNTs and (c) CS/PAA/PEG/PIP/f-MWCNTs.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ID/IG</th>
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<tbody>
<tr>
<td>As-synthesized MWCNTs</td>
<td>1.67</td>
</tr>
<tr>
<td>f-MWCNTs</td>
<td>1.25</td>
</tr>
<tr>
<td>CS/PAA/PEG/PIP/f-MWCNT nanofibre blend</td>
<td>5.10</td>
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impurity of the f-MWCNTs due to attachment of the f-MWCNTs on the electron-deficient carbons of the polymers or nucleophilic reaction of the electron-deficient carbons of the f-MWCNTs with the electron-rich carbons of the polymers.

3.6. Thermogravimetric analysis
TGA results of CS, CS/PAA/PEG/PIP/f-MWCNTs and CS/PAA/PEG/PIP/f-MWCNTs/Ag/Fe nanofibres and their corresponding derivatives plots are presented in Figure 11. The thermal degradation of the as-supplied CS was observed to take place in three steps: the first mass loss (12%) at 32–125°C associated to the loss of water bound in the sample. The second mass loss (66%) at 217–399°C associated to the depolymerization and decomposition of the CS monomers (44). The last weight loss (20%) occurred over a wide temperature range (342–600°C) which corresponds to the complete degradation of CS.

The thermal degradation of CS/PAA/PEG/PIP/f-MWCNTs was observed to take place in five steps. The first mass loss (6%) at 50–117°C was due to the loss of bound water. The second mass loss (33%) with different segments at 118–300°C was assigned to the dehydration and depolymerization of PIP. The different mass loss segments are inherent to the depolymerization and decomposition of stable formed products of PIP during the dehydration and depolymerization. The third (23%) and fourth (11%) mass losses at 451–521 and 544–575°C were associated to the decomposition of thermally stabilized polymers on addition of f-MWCNTs and the rigid, thermally stable products of PIP liberated in the second decomposition step (45). The fifth mass loss (4%) was observed at 709–750°C and was associated to the final decomposition of the polymers and the decomposition of f-MWCNTs. The remaining mass (2%) was ascribed to residual components that could not decompose at that temperature.

The decomposition trend of CS/PAA/PEG/PIP/f-MWCNTs/Ag/Fe nanofibrous composites was found to be similar to that of CS/PAA/PEG/PIP/f-MWCNTs with the slight differences due to the presence of Ag and Fe NPs. The thermal stability of polymeric nanocomposites filled with f-MWCNTs and metallic NPs is known to be higher than those of the polymeric materials without the fillers/additives (46, 47). Hence, the thermal degradation of the polymers was found to increase to 451–573°C on addition of f-MWCNTs, Ag NPs and Fe NPs (Figure 11).

Figure 11. Thermal degradation of CS-based nanofibres and their corresponding derivatives.
3.7 X-ray diffraction analysis
The presence of f-MWCNTs, Ag and Fe NPs in the CS-based nanofibres was confirmed by XRD analysis and the results are presented in Figure 12. The Joint Committee on Powder Diffraction Standards (JCPDS) card values for the following planes (003) and (101) at 2-theta = 25.89° and 43.33° are characteristic diffractions of CNTs (Figure 12(a)). The JCPDS card values for the following planes (111), (400), (311), (511), (533), (711), (911) and (975) at 2-theta = 10.74°, 24.97°, 27.25°, 32.62°, 41.52°, 45.40°, 58.99°, 84.57° are characteristic diffractions of carbon allotropes (Figure 12(b)) (48, 49). The JCPDS card values for the following planes (400), (111), (200), (220), (311), (222) at 2-theta = 24.65°, 38.26°, 44.47°, 64.71° and 77.75°, 81.92° are characteristic diffractions of C and Ag NPs (Figure 12(c)). The JCPDS card values for the following planes (101), (110), (200), (211) at 2-theta = 25.26°, 44.49°, 64.73° and 81.91° are characteristics diffractions of Fe NPs (Figure 12(d)). The diffractions at 2-theta = 24.65° on Figure 12(c) and 2-theta = 25.26° on Figure 12(d) were associated to the diffraction of C in the nanofibres. The diffraction patterns of Ag NPs on Figure 12(d) were observed at the similar planes with no shift of diffraction angles. This suggested that there was no change of chemical surrounding on the Ag NPs in the presence of Fe NPs.

3.8 Swelling tests
The swelling behaviour of the CS-based nanofibres is presented in Figure 13. The swelling rate of all the nanofibres with different degree of cross-linking was found to be high in the first 20 min. The swelling rate decreased after 20 min until equilibrium was reached at 90 min. When CS was cross-linked with GLA at the CS:GLA ratio of 1:0.25, the equilibrium swelling was found to be 122%. When CS was blended with PIP at CS:PIP ratio of 1:0.8 and cross-linked with GLA at CS:GLA ratio of 1:0.25,
the equilibrium swelling was found to be 60%. When CS was cross-linked with GLA at the CS:GLA ratio of 1:1, the equilibrium swelling was found to be 81%. When CS was blended with PIP at CS:PIP ratio of 1:0.8 and cross-linked with GLA at CS:GLA ratio of 1:1, the equilibrium swelling was found to be 38%. It was observed that blending CS with PIP and cross-linked with GLA reduced the swelling behaviour of CS-based nanofibres by 50% with respect to specific cross-linking. This reduction in water uptake of CS based nanofibres on addition of PIP was related to the decreased hydrophilic groups which are the main sources of water uptake (50).

3.9. Tensile tests

Figure 14 shows the stress and the elongation graph of CS-based nanofibres and the effect of addition of f-MWCNTs on the strength of the nanofibres. The load-at-break and maximum load of the CS-based nanofibres were found to be 0.56 and 15.11 N, respectively. Addition of small quantities of f-MWCNTs to CS-based nanofibres was found to increase the load at break and the maximum load to 3.82 and 27.97 N, respectively. The increase in strength of the nanofibres was attributed to the strength associated to the f-MWCNTs. The nanofibres did not show the point of fracture during mechanical testing. This was due to the fact that the nanofibres are materials that are laid down in layers with fine entanglements. They continuously unwind when the tensile stress is applied to them. As the nanofibres unwind, they need less energy to unwind them, hence decreased the tensile strength without showing the point of fracture.
4. Conclusion

CS-based nanofibres were successfully synthesized using an electrospinning technique. Morphology and size of the nanofibres was found to depend on the electrospinning parameters such as voltage, solution flow rate, distance between the collector and the tip of the spinneret as well as the solution concentration. Addition of PIP was found to significantly reduce the swelling of CS-based nanofibres and their morphologies were significantly improved. Tensile strength and the thermal stability of the nanofibres were found to increase with the addition of small quantities of f-MWCNTs. In the previous work, it was reported that the CS-based nanofibres containing Ag and Fe NPs significantly exhibited growth inhibitions of 12 different strains of bacteria, and therefore, could be used as disinfectants during water treatment (5).

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