Studies on electrospun chitosan based nanofibres reinforced with cellulose and chitin nanowhiskers

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INTRODUCTION

Electrospinning has gained wide interest as a unique technique capable of producing polymer nanofibers with diameter in the range of several micrometers down to tens of nanometers[1-3]. In electrospinning, a high voltage is introduced into a polymer solution to produce nanofibres. Decreasing the diameter of the fibres to nanoscale significantly increases the surface area to volume ratio, reduces small diameter and pore size while improving temperature insulation of electrospun nanofibres. Thus, the nanofibres hold promise for uses in wide applications such as composites, biomedical and others[4,5].

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The potential of nanocomposites reinforced with polysaccharide nanowhiskers in various sectors of research and application is attracting enormous investment. For example, the inclusion of chitin and cellulose nanowhiskers in biopolymer matrix has been reported not only to improve the water vapour, but to also to enhance the thermomechanical properties and structural morphology of electrospun nanofibres[6,7].

Chitin is the second most abundant polymer in nature, following cellulose, and is produced from shrimps or crabshells. When deacetylated, chitin is converted into chitosan which has more explored capabilities due to solubility in dilute acids solutions[1]. Therefore, the processability of chitosan makes it possible to be used in electrospinning of nanofibres and reinforced composites.

The aim of the project is to fabricate chitosan nanofibres reinforced with chitin and cellulose nanowhiskers, and also to determine the effect of cellulose and chitin nanowhisker loadings on the morphological integrity and thermomechanical properties of electrospun chitosan nanofibres.

EXPERIMENTAL

Crab shell chitin in the form of flakes was purchased from Sigma-Aldrich GmbH (Germany) and used to produce chitin nanowhiskers (CNW). Microcrystalline cellulose (VIVAPUR® 105), by JRS Pharma was used as the starting material to produce cellulose nanowhiskers (CLW). Cellulose nanowhiskers were produced by the 63% sulphuric acid hydrolysis of microcrystalline cellulose (MCC) using the procedure reported by Bondeson et al[8]. Loadings of concentrations of 1.25 – 5% of CNW and CLW were incorporated into the chitosan (CH) solution and electrospun at 20cm and applied voltage of 15kV (0.75kV/cm), respectively. Nanowhisker and nanofibre characteristics were determined by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR).

RESULTS AND DISCUSSION

The nanowhiskers with spindle-like morphologies and diameter ranges of 10-20nm for chitin and 3-10nm for cellulose were developed as nanocomposite materials for reinforcement. **Figure 1** demonstrates the mostly individual and highly crystalline chitin and cellulose structures.

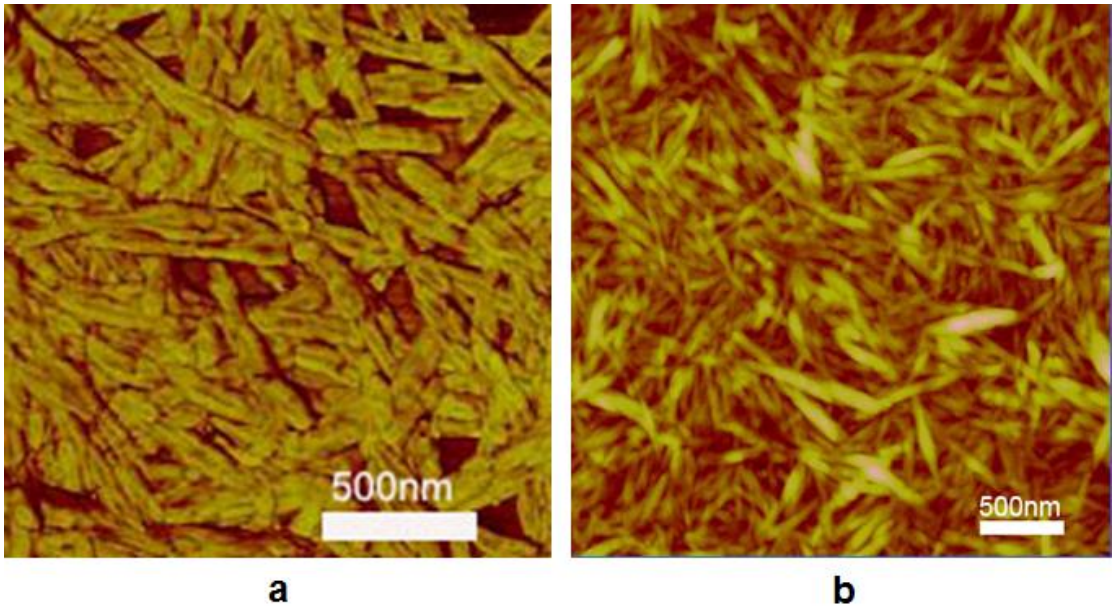

Figure 1 Height images of a) Chitin nanowhiskers and b) Cellulose nanowhiskers obtained using atomic force microscopy.

Figure 2 shows the structural morphology of electrospun nanofibres prepared with 5% CNW and 5% CLW contents. The SEM examination revealed that a homogeneous morphology with potentially good interfacial adhesion seems to have been achieved for the composites studied. When the concentrations of the CH, CH-CNW and CH-CLW solutions were varied, noteworthy changes were observed in the structural morphology and diameter of electrospun nanofibers. These changes were prominent when the CNW and CLW were added to the CH polymer solutions which led to a decrease in fibre diameter.

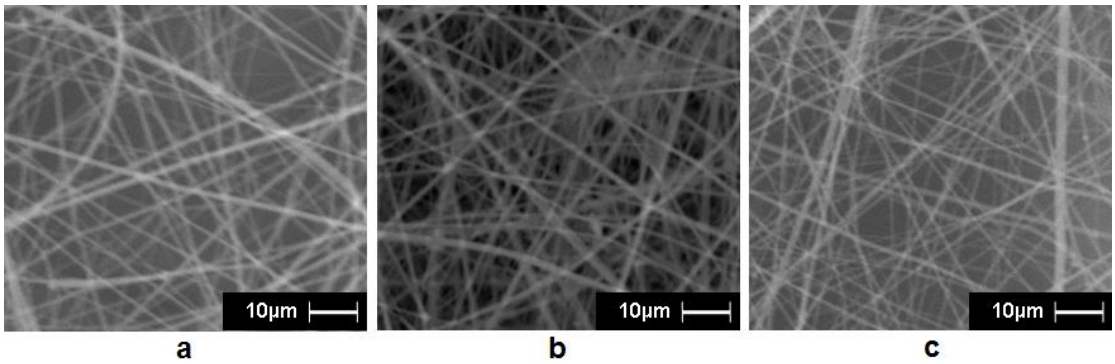

Figure 2 SEM micrographs showing the effect of chitin and cellulose nanowhiskers on the structural morphology and diameter of electrospun nanofibres a) CH b) CH-CNW5 c) CH-CLW5.

Table 1.Relationship between the Concentrations of CH, CNW and CLW and the Fibre Diameter of Electrospun Nanofibres at 20cm and Applied Voltage of 15kV (0.75 kV/cm)

Sample	Concentration (%)			Mean Diameter (nm)
	CH	CNW	CLW	
CH	100			213
CH-CNW5	95	5		143
CH-CNW2.5	97.5	2.5		163
CH-CNW1.25	98.75	1.25		171
CH-CLW5	95		5	160
CH-CLW2.5	97.5		2.5	165
CH-CLW1.25	98.75		1.25	174

Furthermore, in **Table 1**, the average fibre diameter of neat chitosan nanofibres was 213nm, and the CNW loading induced a significant reduction in fibre diameter, at least down to a range of 143 - 171nm for 1.25 - 5% CNW while the 1.25 - 5% of CLW loading caused a decrease down to a range of 160 - 174nm. This is possibly due to structural interactions between CH-CNW as well as CH-CLW that weakens the bonds and hence encourage more stretching and elongation of the jet during electrospinning, thereby causing reduction in the fibre diameter.

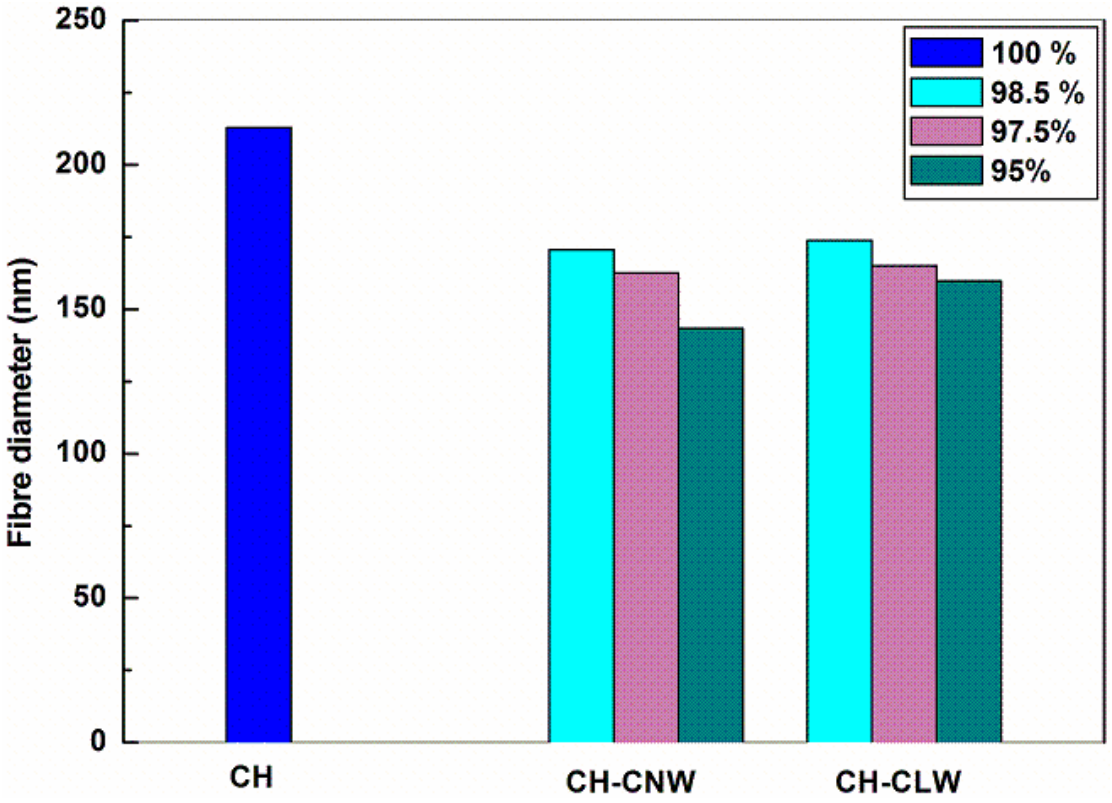

Figure 3 Comparison between concentrations of CH, CH-CNW, CH-CLW and the corresponding average fibre diameter of electrospun nanofibers at 0%, 1.25%, 2.5% and 5% of nanowhisker loadings at 20cm and applied voltage of 15kV (0.75 kV/cm).

The results in **Figure 3** correspond with the results in **Table 1** which indicates a decrease in fibre diameter as the nanowhisker loadings are increased in both CNW and CLW. With further increase in concentrations of CNW and CLW, there is a decrease in fibre diameters of electrospun nanofibres with % reduction illustrated as 33% for higher content of CLW and 25% for higher levels of CNW and with respect to neat chitosan. Also, the trend of higher fibre diameter in CLW was observed when compared to CNW as a result of higher entanglements of the cellulose polymer chain in the solution which yields fibres with larger diameters. This is possibly due to greater resistance of the polymer solution when being stretched as a result of electrical charges on the electrospinning jet.

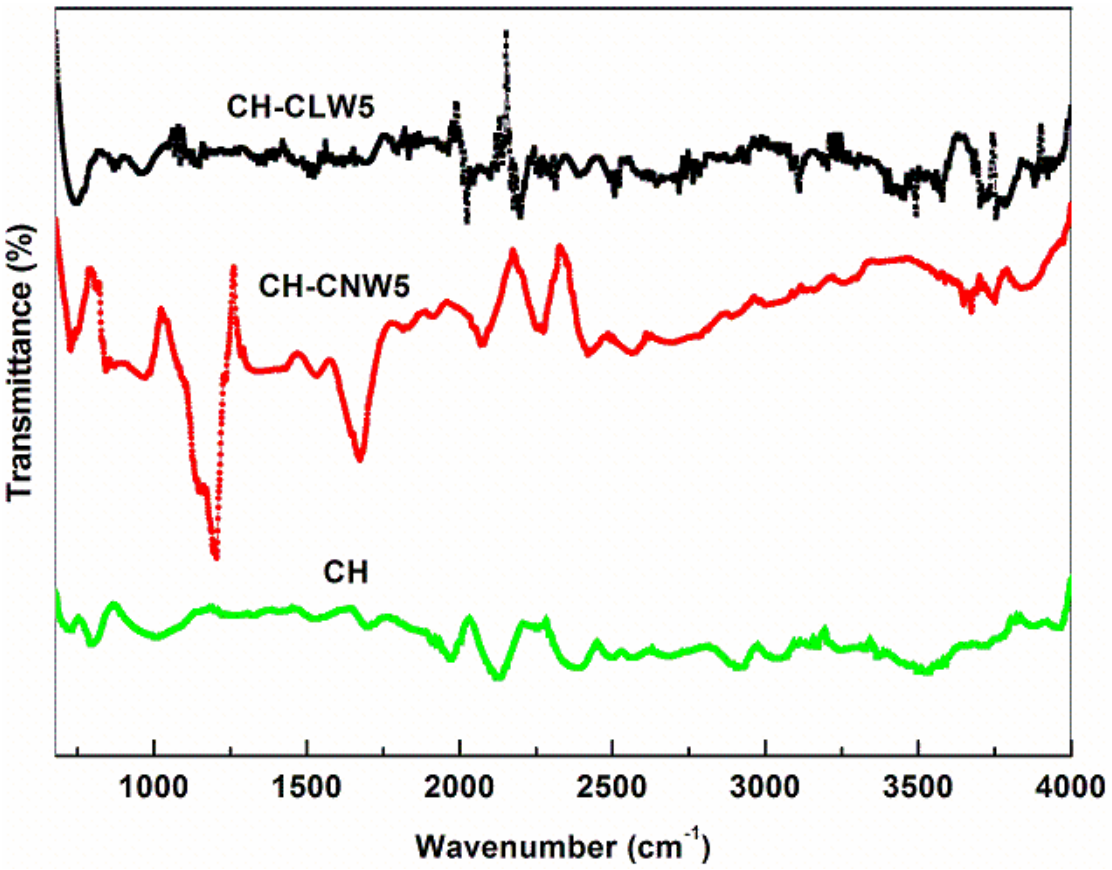

Figure 4 FTIR spectra of the CH, CH-CNW5 and CH-CLW5 electrospun nanofibres.

FTIR spectra were conducted on the electrospun nanofibres of neat chitosan, chitosan-chitin nanowhiskers and cellulose nanowhiskers with 5 wt % nanowhisker content. In comparison, FTIR spectra of the CH, CH-CNW5 and CH-CLW5 nanofibrous mats, it is evident that chitosan is present in both electrospun chitin nanowhiskers and the cellulose nanowhiskers as indicated by its characteristics NH and OH stretch shoulder bands (3640, 3702 and 3649 cm^{-1}, NH stretch; 3506 cm^{-1}, OH stretch). This gives indication that the chitin nanowhiskers as well as the cellulose nanowhiskers are well integrated into the chitosan electrospun nanofibres during electrospinning.

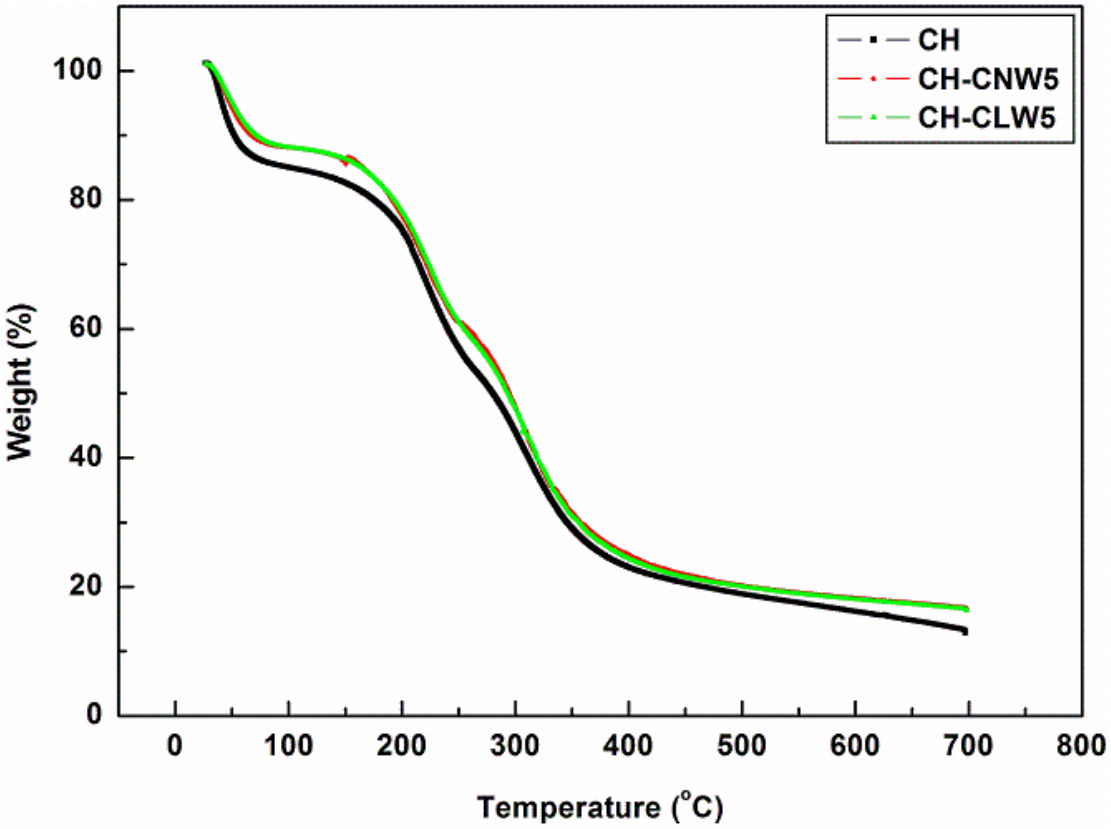

Figure 5 Weight losses in air as a function of temperature in CH, CH-CNW5 and CH-CLW5 electrospun nanofibres.

All samples in **Figure 5** follow a two step degradation pattern with a major degradation occurring around 300°C. This is attributed to degradation and deacetylation of chitosan. Samples with CNW and CLW exhibit higher thermal stability than chitosan. Degradation temp increased by 15-20°C for electrospun nanofibrous membranes with a greater increase for CLW. Increase in thermal stability is due to synergistic effect of combination of CLW with chitosan. Good interaction between CLW and chitosan can also restrict polymer motion during heating resulting in greater thermal stability. However, the highest char residues are obtained for CLW.

CONCLUSIONS

Mostly individualized nanowhiskers were obtained and had 10-20nm for chitin and 3-10nm for cellulose. Chitosan-based nanofibre composite containing chitin and cellulose nanowhiskers as functional components were successfully prepared by electrospinning. The results indicated a good interaction between the matrix and both the chitin and cellulose nanowhiskers, which in turn led to improved structural

morphology, fibre diameter and thermomechanical properties of electrospun nanofibres. The fabrication of electrospun nanofibres containing chitin and cellulose nanowhiskers using electrospinning technique can be considered a viable process that can be utilised to improve the structural morphology and fibre diameter of electrospun nanofibre diameter.

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