

Fabrication of blended chitosan nanofibers by the free surface wire electrospinning

Nawzat D. AlJbour^{1,2}, Mohammad Dalour Hossen Beg^{1,3},
 Jolius Gim bun¹, Mior Ahmad Khushairi Mohd Zahari¹

¹ Center of Excellence for Advanced Research in Fluid Flow (CARIFF), Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Gambang 26300, Kuantan, Malaysia

² Faculty of Pharmacy, Middle East University, Amman, Jordan

³ School of Engineering, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

Corresponding authors: Nawzat D. AlJbour (naljbour@meu.edu.jo); Mohammad Dalour Hossen Beg (dhbeg@yahoo.com)

Received 28 November 2022 ♦ **Accepted** 14 June 2023 ♦ **Published** 10 July 2023

Citation: AlJbour ND, Beg MDH, Gim bun J, Zahari MAKM (2023) Fabrication of blended chitosan nanofibers by the free surface wire electrospinning. *Pharmacia* 70(3): 465–473. <https://doi.org/10.3897/pharmacia.70.e98122>

Abstract

Nanofibers are fibers with diameters in the nanometer range. They are characterized by their high surface area to volume ratio, flexible surface functionalities, and superior mechanical properties. Chitosan is a polycationic polymer which is abundant in nature. Chitosan nanofibers have been widely explored for different potential applications such as wound dressing, tissue engineering, and drug delivery systems. It is difficult to directly spin pure chitosan, due to its high molecular weight, low solubility, and high viscosity. To produce nanofibers, chitosan is commonly blended with other polymers that possess fiber forming capabilities such as polyvinyl alcohol, polycaprolactone, and Polylactic acid. In this study chitosan oligomers of an average molecular weight 15 kDa was blended with the three copolymers at different weight ratios. The fibers were prepared by the free surface wire electrospinning process, and the formed Chitosan nanofibers were characterized by Scanning Electron Microscopy (SEM). SEM results showed that blending chitosan with PLA enhances its spinnability and facilitates uniform and smooth morphology. Blending chitosan with PLA produced nanofibers with better quality, compared to PVA, and PCL.

Keywords

Chitosan, nanofibers, polylactic acid, polycaprolactone, polyvinyl alcohol, wire electrospinning

Introduction

Nanofibers are fibers with diameters in the nanometer range with impeccable features that makes them suitable for various applications. It is well known that reduction in the diameter of materials could impart more desirable features into such material. As such reduction in fiber sizes from micrometres (10–100 μm) to submicron's or nanometres (10×10⁻³–100×10⁻³ μm), would afford them different characteristic features such as larger surface area to volume ratio, increased flexibility towards sur-

face modifications, increased functionalities, and superior mechanical performance (including stiffness and tensile strength). These outstanding properties make polymeric nanofibers ideal candidates for many important applications. In addition, these nanofibers exhibit interesting porosity and structure that could mimic the structure of the extracellular matrix (Son et al. 2014). Some of the notable applications where polymeric nanofibers have gained large interest include fields such as electronics, textile, medical, conductors, enzyme immobilization, nanocomposites, and general chemistry

(Haider et al. 2018). Notably, polymeric nanofiber mats have been reportedly used for the delivery of both hydrophilic and hydrophobic drugs (Song et al. 2018; Xu et al. 2011). Interestingly, the use of nanofibers could offer advantages such as cost effectiveness, ease of production, high encapsulation efficiency, high drug loading capacity, multi drug delivery, and improved controlled drug release profiles.

Production of nanofibers could be through any of the processes such as drawing, self-assembly, phase separation, and electrospinning. Among these methods, electrospinning is of particular interest. In fact, it is being considered as the most cost effective, simple approach to produce ultrafine fibers with a simple set-up. Electrospinning is a progressive method which produces fibers ranging from the submicron range to several nanometres of diameter using a high voltage electrostatic field. Nevertheless, despite the advantages offered by this process, the low throughput has been a serious bottleneck that limits its applications (Wen et al. 2016). Another major limitation is the potential complicated structures which could arise from multiple-fluid spinning processes (Yang et al. 2016; Yu et al. 2016). Interestingly, literature have revealed that the free surface electrospinning system using Nanospider electrospinning technology could help to overcome the challenges associated with conventional electrospinning processes. For example, this technique offers the possibility for continuous and mass production of nanofiber layers (Yalcinkaya 2016).

Chitin and chitosan are polysaccharides obtained from the exoskeleton of arthropods and cell walls of fungi and yeast. They possess excellent biocompatibility and biodegradability, with versatile biological performance such as antimicrobial activity, low immunogenicity, and low toxicity (Murphy et al. 2013; Sainitya et al. 2015). Likewise, these biopolymers possess peculiar amino functionality and two hydroxyl groups which makes it easier for them to be chemically modified. In addition, a host of enzymatically modified products can be obtained from them. Therefore, they are highly desirable in several important applications, such as biomedical, pharmaceutical, and biotechnological applications (Kumar et al. 2014; Dhivya et al. 2015).

Currently, electrospun nanofibers based on chitosan have been widely studied, and various nanofibers with chitosan as the essential component have been produced by electrospinning with reports showing that these materials could be applied in various applications. It is of great advantage to chitosan that it is soluble in most acids, and the protonation of chitosan changes it into a polyelectrolyte in acidic solutions. Notwithstanding, it is difficult to fabricate pure chitosan nanofibers because the application of a high electric field during electrospinning triggers the repulsive forces between ionic groups within the polymer backbone. This would result in the formation of beads instead of fibers (Min et al. 2004). However, different solvents have been combined to prepare spinnable nanofibers of chitosan which produced better

fibrous properties (Ziani et al. 2011; Mendes et al. 2016). In addition, chitosan nanofibers have been prepared by blending chitosan with other spinnable polymers to produce spinnable blends.

The preparation of blended nanofibers helps to solve the problem of chitosan nanofibers formation. In addition, it could lead to synergy between chitosan and the blended polymer. In fact, the blended nanofibers are more advantageous compared to the single electrospun nanofibers, for improving the mechanical, structural antibacterial, biocompatible, and engineered properties of materials (Yalcinkaya 2016).

The significance and novelty of this research is in the use of the free surface wire electrospinning process in the fabrication of chitosan nanofibers. Free surface wire electrospinning process is considered of high potential to solve the problem of mass production accompanying most of the conventional processes used for nanofibers formation. The high productivity in addition to the ease of setting up and clean up give this process superior strength compared to others available techniques. Therefore, fabricating the nanofibers of chitosan using this process is considered of high importance.

The objective of this research is to fabricate chitosan nanofiber mats using the free surface wire electrospinning process. Specifically, chitosan was blended with other polymers such as PVA, PCL, and PLA to improve the structural properties of the produced nanofibers.

Materials and methods

Materials

Low molecular weight chitosan (LMWC), (15 kDa, 100%DDA) was prepared in-house using the acid hydrolysis method by the use of 2M Hydrochloric acid. The produced chitosan was characterized for its degree of deacetylations by the 1st derivative UV method, the viscosity average molecular weight of chitosan was determined using Marck-Houwink Equation. Poly (lactic acid) (PLA) (3052D), poly (caprolactone) (PCL) (23 kDa), and poly (vinyl) alcohol (PVA) (30kDa) which were used as a copolymer for the nanofiber preparation were purchased from Unic Technology Ltd, Taiwan. On the other hand, dichloromethane (99.8%) was purchased from Merck, Germany.

Preparation of the spinning blend

About 9 g of PVA was dissolved in water to prepare a solution of 9 wt% concentration. Then, specific amounts of PCL, and PLA were dissolved in dichloromethane or in the (30:70) mixture of (acetic acid: formic acid) to prepare solutions of 3 wt% PCL, 10% PCL, and 6 wt% PLA. The 15 kDa chitosan was blended with the previously prepared PVA, PCL, and PLA solutions by adding the required amounts of chitosan and kept them under

Table 1. Concentrations of chitosan and copolymers in the spinning blends.

NO	Sample ID	Solvent	Cs Mwt (kDa)	%wt Cs in solution	%wt PVA in solution	%wt PCL in solution	%wt PLA in solution
1	9% PVA	water	15	0	9	–	–
2	3% PCL, 2.5% Cs 15kDa	Dichloromethane	15	2.5	–	3	–
3	10% PCL, 2.5% Cs 15kDa	(acetic acid: formic acid) (30:70)	15	2.5	–	10	–
4	2% PLA	Dichloromethane	15	0	–	–	2
5	4% PLA	Dichloromethane	15	0	–	–	4
6	6% PLA	Dichloromethane	15	0	–	–	6
7	6% PLA, 2% Cs 15 kDa	Dichloromethane	15	2	–	–	6
8	6% PLA, 15% Cs 15 kDa	Dichloromethane	15	15	–	–	6
9	6% PLA, 25% Cs 15 kDa	Dichloromethane	15	25	–	–	6

continuous stirring for 24 h. The composition of the different grades of the prepared spinning blends are shown in Table 1.

Fabrication of chitosan nanofibers using free surface wire electrospinning system (NANOSPIDER)

The electrospinning of chitosan blended nanofibers was conducted at room temperature using Nanospider Electrospinning Machine (Elmarco) (which is shown in Fig. 1) by applying a voltage of 45 kV at a carriage speed of 200 mm/sec, during which the relative humidity in the spinning chamber was kept in the range of 60–69%. The electrospun fibers were collected using a take-up cylinder, on a conveyer which is placed between the two wire electrodes, and at a height of 210 mm from the lower wire.

Morphology of chitosan blended nanofibers

Morphology of the produced fibers was observed through SEM (Hitachi Tabletop TM 3030, Japan). The samples were placed on aluminum stubs after sputtering with a layer of gold, and the diameters of the electrospun fibers were calculated using ImageJ 1.52a software (National Institutes of Health, USA). The average fiber diameters, and diameter distributions was obtained by taking measurement of 100 fibers selected from 3 different samples.

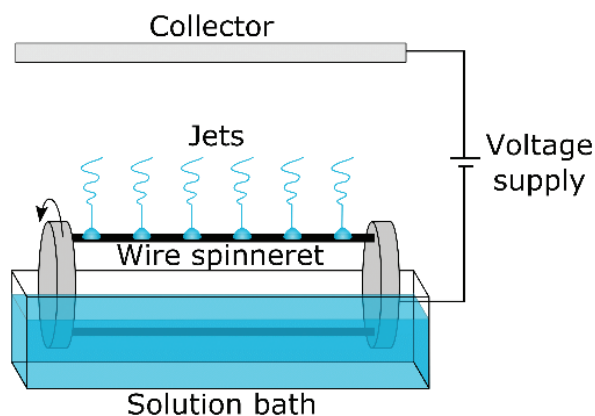


Figure 1. Schematic representation of the wire electrospinning technique.

Fourier Transform Infrared (FTIR) Spectroscopy

The FT-IR analysis is based on the identification of absorption bands associated with the vibrations of functional groups within macromolecules. Herein, dried samples were analysed by taking FTIR spectra in the range of 400 cm^{-1} to 4000 cm^{-1} using a spectrometer (Thermo Scientific Nicolet IS50).

Differential Scanning Calorimetry (DSC)

The DSC analysis is commonly used for the measurement of heat effects on polymers. Generally, this method is used for detecting phase changes such as crystallization, melting, glass transition, and decomposition. In this study, a Perkin Elmer, DSC8000 instrument was used for the DSC analysis. About 2 mg of each powdered sample was placed in closed platinum pans and continuously heated from 30 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 1 $^{\circ}\text{C}/\text{min}$.

Results and discussion

Fabrication of chitosan nanofibers using different copolymers

Chitosan is well known to be among the most naturally abundant biopolymers. However, the strong inter- and intramolecular interactions between the amine groups of chitosan often hinder sufficient chain entanglement. This is a major challenge to prepare chitosan nanofibers with smooth morphology. Previously, the spinnability of chitosan has been reportedly improved by incorporating certain co-spinning agents, including different types of synthetic or natural polymers (Sangsanoh et al. 2006; Mendes et al. 2016). Therefore, different trials have been carried out to prepare chitosan nanofibers.

Herein, chitosan nanofibers were prepared through free surface wire electrospinning process, which is considered a new technique with fewer studies reported. Hence, during the trials, this study relied on previous studies reported about chitosan nanofibers using needle electrospinning process (Haider et al. 2009; Kriegel et al. 2009; Ziani et al. 2011; Koizumi et al. 2017). Firstly, different

solvents were used to prepare chitosan solutions such as TFA, acetic acid with concentrations in the range of 2%–90%. However, these did not work because of different problems relating to conductivity, viscosity, and surface tension. Chitosan was then blended with other spinnable copolymers such as PVA, PCL, and PLA.

Blending with Poly vinyl alcohol (PVA)

Polyvinyl alcohol is one of the polymers previously blended with chitosan and tried for spinning, using the needle electrospinning method. PVA is soluble in water up to 9 wt%, which is a suitable concentration for spinning using the needle electrospinning process. So, in this research, 9 wt% PVA solution was tried for spinning, using the free surface wire electrospinning before blending with chitosan (Huang et al. 2007). The spinning was tried using 50 kv, and 75 kv, and carriage speed of 200 mm/sec.

Fig. 2 shows the SEM image of the fibers prepared from 9 wt% PVA solution. Obviously, the fibers started to form but at an extremely low rate. Therefore, the whole sample could be considered to mainly contain beads and lumps which indicate that during the process, the sample was merely spraying instead of spinning. Due to the inability of PVA to form fibers, it was not blended with chitosan.

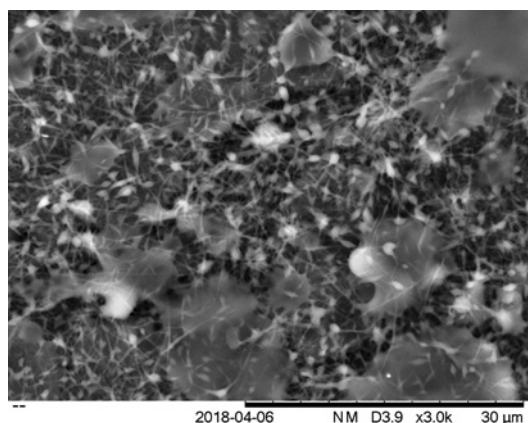


Figure 2. Scanning electron microscope captures of 9 wt% PVA after spinning.

Blending with Polycaprolactone (PCL)

Polycaprolactone (PCL) is considered an ideal candidate that may be incorporated into chitosan, especially due to its salient features. Specifically, PCL is biocompatible, biodegradable, non-toxic and possesses sufficient mechanical properties (Schueren et al. 2011). Therefore, PCL is being investigated for biomedical applications. However, it is highly hydrophobic and does not have cell-recognition sites that can support cell adhesion (Prabhakaran et al. 2008). Interestingly, these properties can be supplied by chitosan. Hence, it is believed that incorporating PCL into chitosan would facilitate the electrospinning process of chitosan. Although PCL is not soluble in water, it is highly soluble in novel solvent such as acetic acid:formic acid mixture in the volume ratio of 3:7. The blend of PCL and chitosan was prepared by

simultaneously dissolving them in a solvent mixture to get a final concentration of 10 wt% PCL with 2.5 wt% Cs (Schueren et al. 2012). Spinning was carried out using the Nanospider under voltage of 50 kv and carriage speed of 200 mm/sec. During the spinning process, fibers began to form and it was obvious to the naked eye as fibers were formed. However, as presented in Fig. 3, the SEM image of the prepared fibers of 10 wt% PCL with 2.5% Cs, revealed that the fibers formed are beaded.

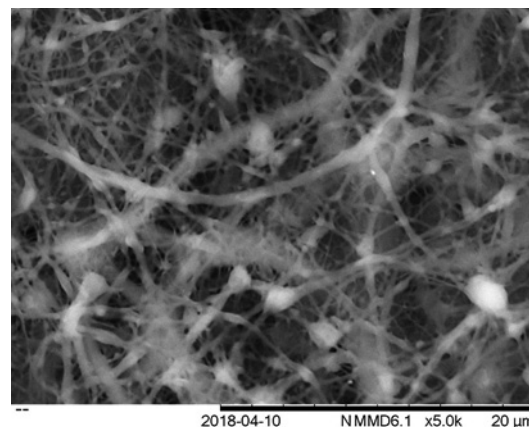


Figure 3. Scanning electron microscope captures of 10 wt% PCL blended with 2.5wt% Cs (Acetic Acid:Formic Acid) (3:7).

It was thought that changing the solvent used may improve the spinnability or improve the quality of the nanofibers formed. Therefore, dichloromethane (DCM) was used to prepare a 3 wt% PCL solution blended with 2.5 wt% Cs, the spinning was carried out under voltage of 45 KV, carriage speed of 200 mm/sec, and 69% humidity. It should be noted that the spinning of organic solvents should be done at high humidity conditions to avoid evaporation. The SEM image of the prepared nanofibers is presented in Fig. 4. As can be seen from the figure, the formed fibers are beaded but much better than those obtained using the solvent mixture (Acetic Acid: Formic Acid, at 3:7). Hence, PCL cannot be fully considered as a suitable solvent to be blended with chitosan to improve its spinnability.

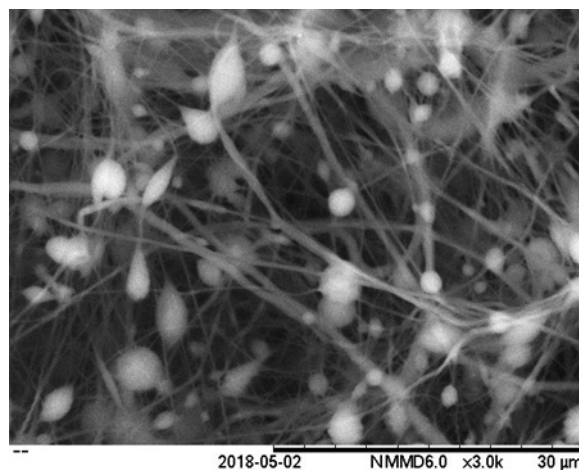


Figure 4. Scanning electron microscope captures of the nanofibers of 3 wt% PCL blended with 2.5 wt% Cs in DCM.

Chitosan blend with polylactic acid (PLA)

Poly lactic acid (PLA) is known to possess good spinning properties because of its surface activity and low viscosity which make it spinnable even at moderate to high concentrations. To determine the spinnable concentration of PLA, solutions with concentrations 2%, 4% and 6% in DCM were prepared and electrospun using a voltage of 45 Kv, and 200 mm/sec carriage speed. Morphologies of the obtained nanofibers are shown in Fig. 5. As can be seen from the figure, the concentrations 2% and 4% PLA formed beaded nanofibrous structure as presented in Fig. 5a and 5b). On the other hand, Fig. 5c shows the morphology of the 6% PLA electrospun nanofibers which exhibits a smooth, neat, and uniform surface. The average diameter is about 158.42 ± 25.87 nm as obtained from the histogram of the fiber size distribution, estimated by the Image j software and shown in Fig. 8. The use of DCM as a solvent helped in getting good nanofibers, where DCM is considered low boiling point solvent (BP is 39.6 °C) compared with other solvents commonly used in electrospinning, such as dimethylformamide (DMF, 153 °C) and acetic acid (Ac.Ac. 118 °C). Solvents should be completely removed from the nanofibers, as the residual solvents may cause adverse effects when nanofibers are used in biomedical applications. Interestingly, this is one of the advantages of using DCM because it can be easily evaporated and then removed from the formed nanofibers (Ogawa et al. 2004).

PLA was then blended with Cs in DCM and tried for nanofibers preparation. Fig. 6 shows the prepared nanofibers of blended solution of 6 wt% PLA with 2 wt% 15 kDa Cs in DCM, under a voltage of 45 V, relative humidity of 69% and carriage speed of 200 mm/sec. The prepared nanofibers were uniformly distributed with an average diameter of about 200 nm. Notably, the presence of chitosan with PLA did not affect the quality of the nanofibers formed and their sizes were still around 200 nm.

Generally, most of the previously reported work on chitosan nanofibers involved acidic solvents such as concentrated acetic acid (Sedghi et al. 2017), trifluoroacetic acid (TFA) Haider et al. 2009), or a mixture of (TFA: DCM) in the ratio of 70:30 (Sangsanoh et al. 2006; Mendes et al. 2016). The main disadvantage of those nanofibers is that they could lose their structure when they come in contact with phosphate buffer saline (PBS, pH 7.4). This could arise from the dissolution of chitosan–acid salts that are usually formed when chitosan is dissolved in acids such as acetic acid or TFA (Sangsanoh et al. 2006). Therefore, the use DCM to dissolve chitosan herein will help to protect the structure of the produced nanofibers during application.

On the other hand, two concentrations of 15 kDa Cs were tried for the formation of nanofibers with 6% PLA. The images in Fig. 7 showed that the fibers formed from 15% 15 kDa Cs, with 6% PLA are considered beaded since large beads and lumps are obvious in the fibrous structure, while at higher concentration of chitosan (25% 15 kDa Cs, with 6% PLA) better beads-free nanofibrous structure was obtained.

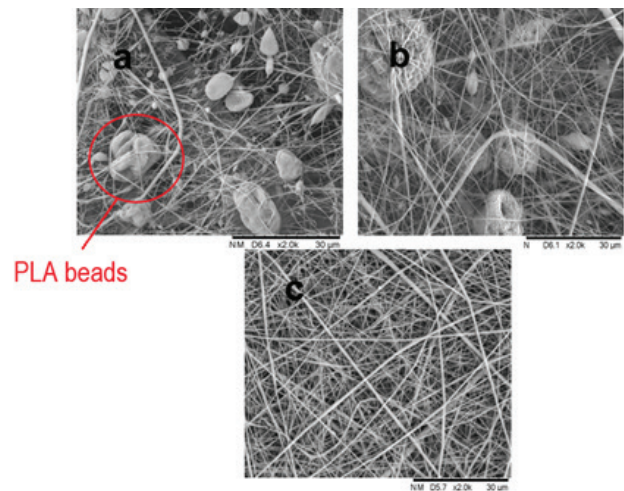


Figure 5. Scanning electron microscope captures of (a) 2wt% PLA (b) 4%PLA (c) 6%PLA all in DCM as solvent.

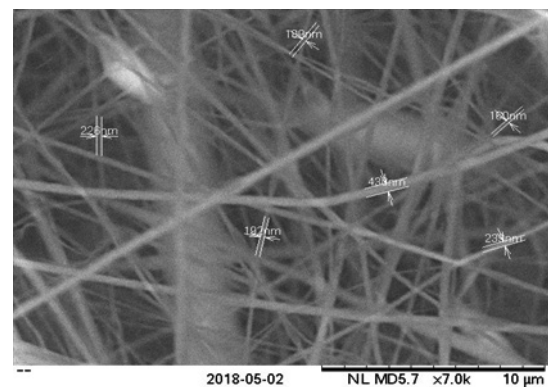


Figure 6. Scanning electron microscope captures with measured sized fibers of the blends of 6wt% PLA with 2wt% Cs 15kDa nanofibers in DCM.

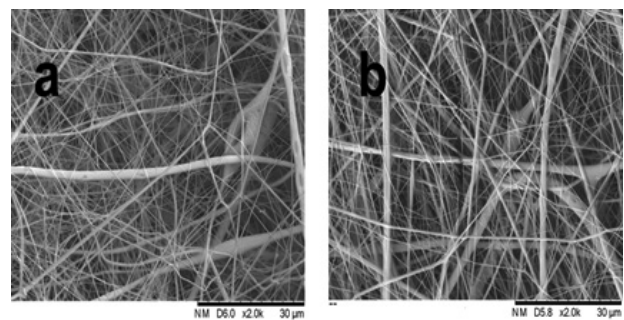


Figure 7. Scanning electron microscope captures of (a) S1(15%Cs 15kDa) (b) S2(25%Cs 15kDa)

The nanofibers diameter distribution diagrams of all prepared nanofibers are illustrated in Figs 8 and 9. Comparing the nanofiber diameters presented in Fig. 9 with the average nano fiber size of PLA (158.42 ± 25.87 nm), it can be inferred that the addition of chitosan to PLA did not cause wide changes in the nanofiber's diameter. On the other hand, the results show that the influence of chitosan concentration on the nanofiber diameter was not significant in the case of 15 kDa Cs, where the size was almost the same in the two concentrations. This could be because solutions of the two different concentrations gave almost the same viscosity and surface tension.

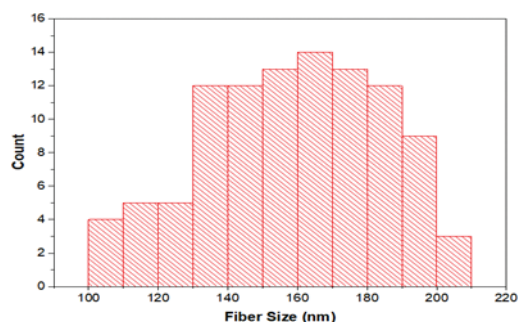


Figure 8. Histogram of the diameter distribution of 6%PLA with an average diameter size of 158.42 ± 25.87 nm.

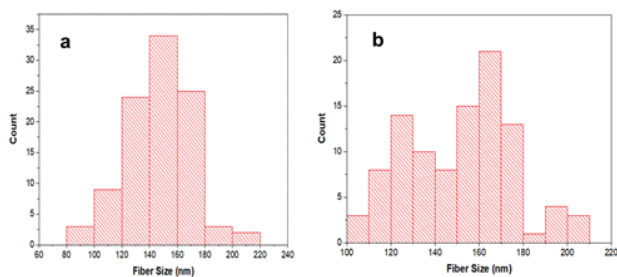


Figure 9. Histogram of the diameter distribution of (a) S1(15% Cs 15kDa) and (b) S2 (25% Cs 15kDa).

Fourier Transforms Infrared Spectroscopy (FTIR)

The inter-molecular interaction between two blended polymers can be investigated through FTIR. The FTIR spectra of the different samples are illustrated in Fig. 10. As illustrated in the figure, the spectra of PLA exhibit some important peaks such as the band around $2999\text{--}2850\text{ cm}^{-1}$ which is attributed to C-H stretching (Olabode et al. 2015). On the other hand, the peak at 1750 cm^{-1} represents the stretching vibration of C=O groups from the carboxylic acid and ester groups of PLA. The peak at 1455 cm^{-1} represents the characteristic stretching of -

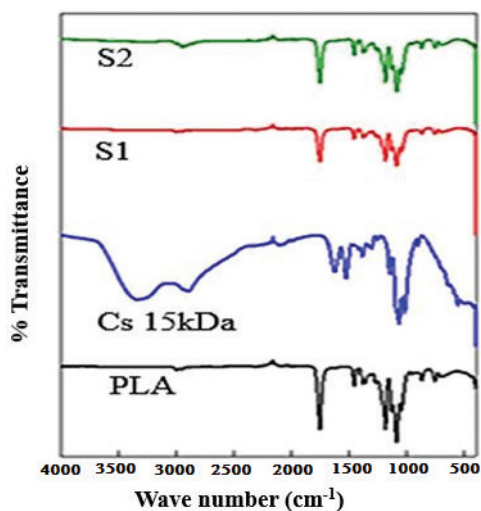


Figure 10. FTIR spectra of PLA, Cs 15kDa, S1(15%Cs 15kDa) and S2(25%Cs 15kDa).

CH_3 , whereas the C-H deformational peak can be seen at 1375 cm^{-1} (Akindoyo et al. 2015). The major peaks available in the structure of chitosan include the peak around 3424 cm^{-1} which represents the N-H stretching. On the other hand, the peak representing the bending of the NH_2 group appears around $1624\text{--}1629\text{ cm}^{-1}$.

Notably, all peaks assigned to the saccharide structures appeared, where the peak around 2890 cm^{-1} represents the C-H stretching peak, 1150 cm^{-1} represents the C-N stretch peak, while the peak at 1320 cm^{-1} is assigned to C-O stretching (Wang et al. 2006; Athamneh et al. 2013).

Table 2. The characteristic FTIR transmittance peaks of PLA, 15 kDa Cs, and PLA-Cs 15 kDa nanofibers.

Sample	Wavenumber (cm^{-1})	Vibrational Mode
PLA	2900	C-H stretching
	1750	C=O stretching
	1455	CH_3 stretching
	1375	C-H deformational peak
Chitosan	3424	N-H stretching
	1625	NH_2 bending
	2890	C-H stretching
	1150	C-N stretching
	1320	C-O stretching
6%PLA, 15%Cs 15kDa & 6%PLA, 25%Cs 15kDa	1750	C=O stretching
	3424	N-H stretching

It is noteworthy that some distinct changes occurred in the FTIR spectra of chitosan-PLA nanofibers as illustrated in Fig. 10. Specifically, the FTIR spectra of all prepared grades of chitosan-PLA nanofibers revealed reduced intensity of the C=O stretching peak at 1750 cm^{-1} , as well as the reduction in the intensity of N-H stretching peak of chitosan. This is indication of interactions between the NH_2 groups of chitosan molecule and the carboxylic acid functional groups of PLA. Significantly, the reduction of the C=O peak was less when using higher concentration of chitosan (25%). This suggests that the reaction between chitosan and PLA was not complete. This low reduction in C=O peak intensity could be due to possible change in the conformation of chitosan, into a helical structure as the concentration increases. As such, more NH_2 groups will be hidden within the chains such that only a smaller number of NH_2 are available to interact with PLA. This would result in decreased interaction between PLA and chitosan. Table 2 summarizes the major peaks in the FTIR spectra of PLA, 15 kDa Cs, and Cs-PLA nanofibers.

Differential Scanning Calorimetry (DSC) Analysis

The DSC analysis helps to investigate the influence of chitosan molecular weight and concentration on the glass transition, crystallization, and melting phenomena of chitosan-PLA nanofibers. The DSC thermograms of the chitosan-PLA nanofibers are illustrated in Fig. 11. Obviously, the figure reveals distinct successive transition regions.

The endothermic transitions represent the glass transition temperature (T_g), and the melting temperature (T_m). On the other hand, the exothermic transition represents the crystallization temperature, (T_c). Close observation of the curves shows that there is a slight right shift in the T_g of PLA (64 °C), following the incorporation of chitosan in all grades of the blended chitosan-PLA nanofibers. Chitosan is well known to have a rigid structure, with glass T_g of around 203 °C (Sakurai et al. 2000). Therefore, the right shift in T_g of PLA in the blends indicate partial miscibility between PLA and chitosan (Shuai et al. 2001; Suyatma et al. 2004). In another vein, around the T_g of polymers, the molecular chains often gain more flexibility and mobility (Jaszkiwicz et al. 2014). Therefore, the shift in the glass transition temperature indicates delay in the free mobility of PLA chains, which can be attributed to restrictions imposed by chitosan on the molecular chain mobility of PLA. This might have retarded the cooperative motions of its chains, thereby inducing an increase in the T_g (Liu et al. 2013).

Generally, the T_g values may be affected by the size of the side groups and the chain mobility. However, it is interesting to know that the T_g obtained herein are comparable to what was previously reported in previous studies (Cai et al. 2010; Au et al. 2012; Pachon et al. 2014). On the other hand, the T_m values show that the endothermic heat in the thermogram of chitosan-PLA nanofibers decreased after incorporating chitosan into the blends. Chitosan is an amorphous polymer and might have interfered with the formation of crystals in the structure of PLA in the chitosan-PLA blend. Hence, multi peaks can be seen in the melting peaks of chitosan-PLA nanofibers. Notably, the multiple peaks in the curve of PLA indicate that there is a different crystalline structure of PLA in the blends after electrospinning, which agrees with what was reported in a previous study (Au et al. 2012).

On the other hand, rigid chitosan in the 15% 15 kDa Cs, and 25% 15 kDa Cs could affect the formation crystalline structure of PLA during nucleation and crystallization. Therefore, this observation can be attributed to the amorphous nature of chitosan which might have retarded the rate of crystallization, thereby generating imperfect crystals (Sakurai et al. 2000). Summary of the DSC parameters such as T_g and T_m of PLA and Chitosan-PLA blended nanofibers are summarized in Table 3.

Conclusion

PLA prove to be more suitable and appropriate polymer to blend with chitosan, compares to PVA and PCL. Chi-

References

Akindoyo JO, Beg MDH, Ghazali SB, Islam MR, Mamun AA (2015) Preparation and characterization of poly (lactic acid)-based composites reinforced with poly dimethyl siloxane/ultrasound-treated oil palm empty fruit bunch. *Polymer-Plastics Technology and*

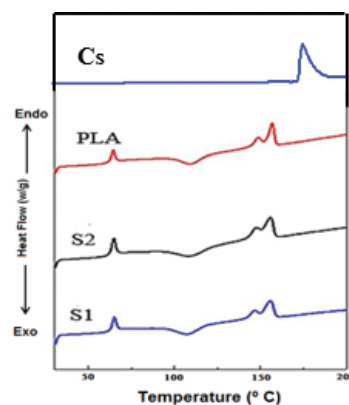


Figure 11. DSC thermograms of Chitosan, PLA, S1 (15%Cs 15kDa), and S2 (25% Cs 15kDa).

Table 3. Summary of glass transition temperature, T_g , and melting temperature T_m , of the different prepared nanofibers.

Sample ID	T_g (°C)	T_m (°C)
PLA (100%PLA)	64.44	T_{m1} : 148.6
		T_{m2} : 156.82
S1 (15% 15 kDa Cs)	63.84	T_{m1} : 146.51
		T_{m2} : 155.69
S2 (25% 15 kDa Cs)	64.88	T_{m1} : 147.07
		T_{m2} : 155.93

tosan-PLA blended nanofibers were successfully prepared by the free surface wire electrospinning process, which is considered advantageous, compared to the needle electrospinning process. The free surface wire electrospinning was found to be suitable for producing large layers of the nanofibers with high production rates. In addition, this method is practical because the clean-up and maintenance procedures are not complicated. Chitosan-PLA nanofibers were prepared using the fully deacetylated chitosan with average molecular weights of 15 kDa. The low molecular weight of chitosan enhances its spinnability since solutions with higher concentrations and lower viscosities could be prepared. The lower molecular weight of 15 kDa chitosan was more suitable to produce the blended nanofibers.

Acknowledgements

The authors are grateful to the Middle East University, Amman, Jordan for the financial support granted to cover the publication fee of this research article.

The authors would like to thank ministry of Higher Education Malaysia for providing funding for this project through Fundamental Research Grant Scheme (FRGS/1/2019/TK05/UMP/02/13) (University reference RDU1901176).

Engineering 54(13): 1321–1333. <https://doi.org/10.1080/03602559.2015.1010219>

Athamneh N, Tashtoush B, Qandil A, Al-Tanni B, Obaidat A, Al-Jbour N, Badwan A (2013) A new controlled-release liquid delivery system

- based on diclofenac potassium and low molecular weight chitosan complex solubilized in polysorbates. *Drug Development and Industrial Pharmacy* 39(8): 1217–1229. <https://doi.org/10.3109/03639045.2012.707205>
- Au HT, Pham LN, Vu THT, Park J (2012) Fabrication of an antibacterial non-woven mat of a poly (lactic acid)/chitosan blend by electrospinning. *Macromolecular Research* 20(1): 51–58. <https://doi.org/10.1007/s13233-012-0010-9>
- Cai Zx, Mo XM, Zhang KH, Fan LP, Yin Al, He Cl, Wang HS (2010) Fabrication of chitosan/silk fibroin composite nanofibers for wound-dressing applications. *International Journal of Molecular Sciences* 11(9): 3529–3539. <https://doi.org/10.3390/ijms11093529>
- Dhivya S, Saravanan S, Sastry T, Selvamurugan N (2015) Nanohydroxyapatite-reinforced chitosan composite hydrogel for bone tissue repair in vitro and in vivo. *Journal of Nanobiotechnology* 13(1): 40. <https://doi.org/10.1186/s12951-015-0099-z>
- Gómez-Pachón E, Vera-Graziano R, Campos RM (2014) Structure of poly (lactic-acid) PLA nanofibers scaffolds prepared by electrospinning. Paper presented at the IOP Conference Series: Materials Science and Engineering 59: 012003. <https://doi.org/10.1088/1757-899X/59/1/012003>
- Haider S, Park SY (2009) Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu (II) and Pb (II) ions from an aqueous solution. *Journal of Membrane Science* 328(1–2): 90–96. <https://doi.org/10.1016/j.memsci.2008.11.046>
- Haider A, Haider S, Kang IK (2018) A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology. *Arabian Journal of Chemistry* 11(8): 1165–1188. <https://doi.org/10.1016/j.arabjc.2015.11.015>
- Huang XJ, Ge D, Xu ZK (2007) Preparation and characterization of stable chitosan nanofibrous membrane for lipase immobilization. *European Polymer Journal* 43(9): 3710–3718. <https://doi.org/10.1016/j.eurpolymj.2007.06.010>
- Jaskiewicz A, Bledzki A, Van Der Meer R, Franciszcak P, Meljon A (2014) How does a chain-extended polylactide behave?: a comprehensive analysis of the material, structural and mechanical properties. *Polymer Bulletin* 71(7): 1675–1690. <https://doi.org/10.1007/s00289-014-1148-8>
- Koizumi R, Azuma K, Izawa H, Morimoto M, Ochi K, Tsuka T, Okamoto Y (2017) Oral administration of surface-deacetylated chitin nanofibers and chitosan inhibit 5-fluorouracil-induced intestinal mucositis in mice. *International Journal of Molecular Sciences* 18(2): 279. <https://doi.org/10.3390/ijms18020279>
- Kriegel C, Kit K, McClements DJ, Weiss J (2009) Electrospinning of chitosan–poly (ethylene oxide) blend nanofibers in the presence of micellar surfactant solutions. *Polymer* 50(1): 189–200. <https://doi.org/10.1016/j.polymer.2008.09.041>
- Kumar JP, Lakshmi L, Jyothsna V, Balaji D, Saravanan S, Moorthi A, Selvamurugan N (2014) Synthesis and characterization of diopside particles and their suitability along with chitosan matrix for bone tissue engineering in vitro and in vivo. *Journal of Biomedical Nanotechnology* 10(6): 970–981. <https://doi.org/10.1166/jbn.2014.1808>
- Liu M, Zhang Y, Zhou C (2013) Nanocomposites of halloysite and polylactide. *Applied Clay Science* 75: 52–59. <https://doi.org/10.1016/j.clay.2013.02.019>
- Mendes AC, Gorzelanny C, Halter N, Schneider SW, Chronakis IS (2016) Hybrid electrospun chitosan-phospholipids nanofibers for transdermal drug delivery. *International journal of Pharmaceutics* 510(1): 48–56. <https://doi.org/10.1016/j.ijpharm.2016.06.016>
- Min BM, Lee SW, Lim JN, You Y, Lee TS, Kang PH, Park WH (2004) Chitin and chitosan nanofibers: electrospinning of chitin and deacetylation of chitin nanofibers. *Polymer* 45(21): 7137–7142. <https://doi.org/10.1016/j.polymer.2004.08.048>
- Murphy CM, O'Brien FJ, Little DG, Schindeler A (2013) Cell-scaffold interactions in the bone tissue engineering triad *Eur. Cells Mater* 26: 120–132. <https://doi.org/10.22203/eCM.v026a09>
- Ogawa K, Yui T, Okuyama K (2004) Molecular conformations of chitin and chitosan. *Foods and Food Ingredients Journal of Japan* 209: 311–319.
- Olabode AJ (2015) Oil Palm Empty Fruit Bunch (EFB) Fiber Reinforced Poly (lactic) Acid Composites: Effects of Fiber Treatment and Impact Modifier. UMP.
- Prabhakaran MP, Venugopal JR, Chyan TT, Hai LB, Chan CK, Lim AY, Ramakrishna S (2008) Electrospun biocomposite nanofibrous scaffolds for neural tissue engineering. *Tissue Engineering Part A* 14(11): 1787–1797. <https://doi.org/10.1089/ten.tea.2007.0393>
- Sainitya R, Sriram M, Kalyanaraman V, Dhivya S, Saravanan S, Vairamani M, Selvamurugan N (2015) Scaffolds containing chitosan/carboxymethyl cellulose/mesoporous wollastonite for bone tissue engineering. *International Journal of Biological Macromolecules* 80: 481–488. <https://doi.org/10.1016/j.ijbiomac.2015.07.016>
- Sakurai K, Maegawa T, Takahashi T (2000) Glass transition temperature of chitosan and miscibility of chitosan/poly (N-vinyl pyrrolidone) blends. *Polymer* 41(19): 7051–7056. [https://doi.org/10.1016/S0032-3861\(00\)00067-7](https://doi.org/10.1016/S0032-3861(00)00067-7)
- Sangsanoh P, Supaphol P (2006) Stability improvement of electrospun chitosan nanofibrous membranes in neutral or weak basic aqueous solutions. *Biomacromolecules* 7(10): 2710–2714. <https://doi.org/10.1021/bm060286l>
- Sedghi R, Shaabani A, Mohammadi Z, Samadi FY, Isaei E (2017) Biocompatible electrospinning chitosan nanofibers: a novel delivery system with superior local cancer therapy. *Carbohydrate Polymers* 159: 1–10. <https://doi.org/10.1016/j.carbpol.2016.12.011>
- Shuai X, He Y, Asakawa N, Inoue Y (2001) Miscibility and phase structure of binary blends of poly (l-lactide) and poly (vinyl alcohol). *Journal of Applied Polymer Science* 81(3): 762–772. <https://doi.org/10.1002/app.1493>
- Son YJ, Kim WJ, Yoo HS (2014) Therapeutic applications of electrospun nanofibers for drug delivery systems. *Archives of Pharmacal Research* 37(1): 69–78. <https://doi.org/10.1007/s12272-013-0284-2>
- Song B, Wu C, and Chang J (2012) Controllable delivery of hydrophilic and hydrophobic drugs from electrospun poly (lactic-co-glycolic acid)/mesoporous silica nanoparticles composite mats. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 100(8): 2178–2186. <https://doi.org/10.1002/jbm.b.32785>
- Suyatma NE, Copinet A, Tighzert L, Coma V (2004) Mechanical and barrier properties of biodegradable films made from chitosan and poly (lactic acid) blends. *Journal of Polymers and the Environment* 12(1): 1–6. <https://doi.org/10.1023/B:JOOE.0000003121.12800.4e>
- Van der Schueren L, De Schoenmaker B, Kalaoglu ÖI, De Clerck K (2011) An alternative solvent system for the steady state electrospinning of polycaprolactone. *European Polymer Journal* 47(6): 1256–1263. <https://doi.org/10.1016/j.eurpolymj.2011.02.025>
- Van der Schueren L, Steyaert I, De Schoenmaker B, De Clerck K (2012) Polycaprolactone/chitosan blend nanofibers electrospun from an

- acetic acid/formic acid solvent system. *Carbohydrate Polymers* 88(4): 1221–1226. <https://doi.org/10.1016/j.carbpol.2012.01.085>
- Wang A, Ao Q, Cao W, Yu M, He Q, Kong L, Zhang X (2006) Porous chitosan tubular scaffolds with knitted outer wall and controllable inner structure for nerve tissue engineering. *Journal of Biomedical Materials Research Part A* 79(1): 36–46. <https://doi.org/10.1002/jbm.a.30683>
- Wen HF, Yang C, Yu DG, Li XY, Zhang DF (2016) Electrospun zein nanoribbons for treatment of lead-contained wastewater. *Chemical Engineering Journal* 290: 263–272. <https://doi.org/10.1016/j.cej.2016.01.055>
- Xu J, Jiao Y, Shao X, Zhou C (2011) Controlled dual release of hydrophobic and hydrophilic drugs from electrospun poly (l-lactic acid) fiber mats loaded with chitosan microspheres. *Materials Letters* 65(17–18): 2800–2803. <https://doi.org/10.1016/j.matlet.2011.06.018>
- Yalcinkaya F (2016) Preparation of various nanofiber layers using wire electrospinning system. *Arabian Journal of Chemistry* 12(8): 5162–5172. <https://doi.org/10.1016/j.arabjc.2016.12.012>
- Yang C, Yu DG, Pan D, Liu XK, Wang X, Bligh SA, Williams GR (2016) Electrospun pH-sensitive core-shell polymer nanocomposites fabricated using a tri-axial process. *Acta Biomaterialia* 35: 77–86. <https://doi.org/10.1016/j.actbio.2016.02.029>
- Yu DG, Yang C, Jin M, Williams GR, Zou H, Wang X, Bligh SA (2016) Medicated Janus fibers fabricated using a Teflon-coated side-by-side spinneret. *Colloids and Surfaces B: Biointerfaces* 138: 110–116. <https://doi.org/10.1016/j.colsurfb.2015.11.055>
- Ziani K, Henrist C, Jérôme C, Aqil A, Maté JJ, Cloots R (2011) Effect of nonionic surfactant and acidity on chitosan nanofibers with different molecular weights. *Carbohydrate Polymers* 83(2): 470–476. <https://doi.org/10.1016/j.carbpol.2010.08.002>