Characterization of PVA/chitosan Nano Fiber Membrane and Increasing Mechanical Properties with Cross-Linking by Heating

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Abstract: A stable Chitosan (Cs)/Poly(vinyl alcohol) (PVA) nanofiber membrane was made for an aqueous environment. To achieve this, using the design of the experiments with the surface response method (RSM) and central composite design (CCD) approach. We obtained a suitable concentration of polymers solution and the ratio of the Cs:PVA combination. The cross-linking temperature was optimized.

Key-Words: Nanofiber, cross-linking, heating, PVA/chitosan, mechanical properties, electrospinning process, design–expert.

1 Introduction

Chitin is the second most abundant natural polysaccharide that is made by a number of organisms. Chitin is known as major structural component of the exoskeletons of arthropods and the cell walls of fungi and yeasts. However, sea food industry wastes such as crabs, shrimps and shellfish are the main sources of commercial chitin [1]. Since the chitin is not soluble in common solvents readily, Often it will convert to de-acetylation form; chitosan . Chitin and chitosan biocompatible polymers are, biodegradable and non-toxic antimicrobial properties and high hydrophobicity [2]. Due to the high solubility of chitosan in acidic solutions, neutral and alkaline, chitosan is more useful than chitin. Today nanofibers due to having special properties such as high specific surface area and high porosity with small pore size, has been much attention for a variety of applications [3]. Many researchers have been focused on the biomedical applications of fibrous and porous structures, such as drug delivery, wound healing, medical prostheses, pharmaceutical composition tissue engineering scaffolds [4]. Electrospinning method is a promising technique for the production of continuous fibers with nanoscale diameter, in this process used of high voltage electric field to polymer solution. Chitosan nanofibers for tissue engineering have been used extensively as the nano-scaffolds. often in this method, Used of the Aluminium sheet as nano-scaffolding collector, but nanofibers Separating from on the metal sheet, especially chitosan nanofibers is very difficult because nanofibers delicacy and fragility. To enhance stability and improve the mechanical properties, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used [5]. Schiffman et al [6,7] for carboxymethyl chitin/ polyvinyl alcohol (PVA) crosslinking in addition to glutaraldehyde vapor, used of heat treatment. Due to its high efficiency in production, electronics have converted decalcify into one of the most important types of nanostructures [8]. Recently, the imitation of natural tissue in vitro has given special attention to the electrostatic method according to the potential of fiber structure with a diameter in the range close to that of collagen in an extracellular matrix of about 130-30 nm [9]. Types of electrospinning with the application of tissue engineering are: Conventional Electrospinning: the electrospinning process involves the use of a high voltage between a syringe filled with a polymer solution and a collector mounted at a fixed distance. Under specific voltage conditions, polymer depletion rates, and distance, a large potential difference over the surface elasticity of the polymer droplets over the needle tip, and a fluid jet out of the needle is extracted and whipped onto the collector [10]. Emulsion electrospinning: emulsion electrospinning is a process for the production of nanofibres with a brain-shell structure with various medical applications [11]. Emulsion electrospinning fibers can be produced with a wide range of porosity, and with the precise control of compounds and moisture in the production process, the physical and chemical potential of these fibers can be strengthened in pharmaceutical applications [12]. Agathe et al. [13] released the successful application of emulsion electrospinning to encapsulate the highly volatile smell of lemon in polyvinyl alcohol (PVA), which showed that emulsion electrospinning, unlike coaxial processes, were scalable and the result of multiple applications as a non-corrosive structure for packaging food or aromatic textiles can be promoted by promoting the release of perfume. Coaxial electrospinning: Coaxial electrospinning is, in fact, a modified classical technique that allows the production of micro and nanofibers with a core and shell structure [14]. Electrospinning without nozzle: In electrospinning without nozzles, instead of producing a jet of polymer from the tip of a needle, tens to hundreds of jets form a free surface of a polymer solution. Simm et al. [15] showed that electrospinning without a nozzle could significantly increase the fiber production rate. The needless electrospinning process used in research by Kolos et al. [16]. The existence of sharp tips on the surface without nozzles was used in this design and their results showed that increasing the process efficiency depends on: the density of the Taylor cones, which are the basis of jet formation, the type of polymer, and the size of the sharp points. Eva et al. [17] used a rotary submerged cylinder within a polymer solution, their design benefits include: continuous fiber production, high production capacity and ease of maintenance. Nowadays, various types of surfaces have been invented for non-nozzle electrospinning. Yarin et al. [18] used a two-layer system, the lower layer of a suspended subsurface, and the upper layer of a polymer solution in the presence of a magnetic field. Nano-fiber fabrication groups can be increased by adding nanoparticles, biomaterials, pharmaceutical powders, bacterial substances or metal oxides to a polymer solution or suspension of fibers within a nanocomposite. Polymer blends are physical blends with different polymer structures or copolymers interacting with secondary forces without covalent bonding [19]. Blend electrospinning: the blend electrospinning method improves the functional properties of nanofibers. For example, Carla et al. [20] succeeded for the first time in the electrospinning of cyanobacterial polysaccharides and PVA, their results showed that the product of nanofiltration has better mechanical tensile properties and greater resistance to collapse, as well as metal lacquer, thermal properties and the mechanical properties of membranes developed using cyanobacter polysaccharides indicate the potential for acceptance for filtration purposes. To provide electrospinning conditions for hard and impossible electrospinning polymers is to combine them with synthetic polymers. Mixing of natural polymer alginate with synthetic polymer PVA was performed with the aim of increasing the mobility of the polymer chains during the electrostatic process and increasing the thermal stability above 350 °C by Shahidul et al. [19] and the results showed that the mixing of these two polymers improved the mechanical properties and thermal resistance of nanofibers. This method can be used to control and adjustment the thermal sensitivity of nanofibres, Yu et al. [21] using a new blend electrospinning method, and from PCL as the core and Polymer-sensitive polyethylene glycol poly (N-isopropyl acrylamide) as a nanofiber shell produced a temperature sensitive product of 40-37 °C. One of the ways to increase the physical strength of the fibers is to optimize the mass values of the mixing of polymers in the mixing electrode. For example, hydroxyapatite (HA) is used as an inorganic and biodegradable material for fiber reinforcement in bone tissue engineering scaffolds. [22]. Zhang et al. [23] tested the tensile strength of the poly (DL-lactic acid) (PDLLA) and poly (D, L-lactic-co-glycolic acid) (PLGA) nanofibers in different amounts of composition , Their results showed that with the addition of PLGA in the range of 50%, the tensile strength of the membrane increases. In this research, nanofibers were produced by mixing different proportions of chitosan and water. And the goal was to achieve an optimal combination with mechanical strengthyou can see for the title of the paper you must use 16pt, Centered, Bold, Times New Roman. Leave one blank line and then type AUTHORS' NAMES (in Capital, 12pt Times New Roman, centered), Department (in 12pt Times New Roman, centered), University (in 12pt Times New Roman, centered), Address (in 12pt Times New Roman, centered), COUNTRY (in Capital, 12pt Times New Roman, centered). Then you must type your e-mail address and your Web Site address (both in 12pt Times New Roman, centered).

2 Material

Chitosan (average Mw 200,000) and poly(vinyl alcohol) (aver-age Mw 72,000) were obtained from Sigma–Aldrich. Acetic acid was purchased from Merck. Deionized water was used for all tasks.lease, leave two blank lines between successive sections as here.

3 Methodology and Experimental Design

In this research, the experiments were designed using the Design–Expert-11 software. The surface response approach was used with central composite design (CCD) method. Table 1 summarizes these basic items of this design.

Table 1: The introduction of variables and call the Design of Experiments.

Variable	Coded	Coded level			
		Low	High	+α	-α
CS concentration (wt%)	X_1	4.75	8.25	3	10
PVA concentration (wt%)	X_2	4.5	11.5	1	15
Cs percentage (V/V%)	X_3	60	80	50	90
Cross-link temperature (°C)	X_4	75	125	50	150
Swelling (%)	Y1	Responses			
Weight (mg)	Y2				

Two responses to choose the best conditions nanofibers were considered: Swelling (%) that it was related to the stability of nanofibres under water for 2h and weight of 10 mm × 10 mm of a nanofibers piece that produced in 1h. This experimental design offered 30 runs.

3.1 Preparation of PVA/Chitosan

The Chitosan and PVA solutions were initially prepared separately by dissolving Chitosan in acetic acid (2, v/v%) and PVA in deionized water at 45 ˚C and 65 ˚C respectively for 15 h on the magnetic Heater stirrer. Concentration of Cs and PVA at solutions and blending of Cs and PVA were obtained according to experiment design pattern based on weight percent (wt%) or weight-weight percentage and volume/volume percentage (V/V%), respectively. Blending done in 55 ˚C for 24h on the heater stirrer.

3.2 Electrospinning Process

In this research the prepared solution was loaded into 10 (1 mL) plastic syringes equipped with a syringe needle. This plastic syringe was placed on the programmable syringe pump to control the solution flow rate. The collector was coated by a non-woven polyester web and Chitosan/PVA nanofibers were produced on this web basis. Then, a high D.C. voltage was applied between the needles and the collector which was coated by polyester non-woven web. This process was performed at a voltage of 18 kV, with a tip-collector distance of 14.5 cm and flow rate of 0.5 ml/h (Fig. 1).

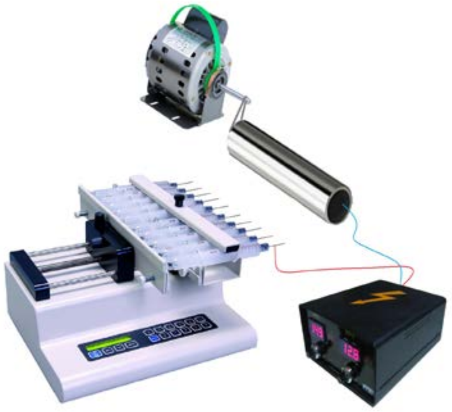


Fig. 1 Schematic of the electrospinning process.

3.3 Cross-linking by Heating

According to experiment design pattern the product was then heated in the oven at 50-150˚C for 15 h and was used for cross-linking of the PVA/chitosan nanofiber membrane to improve its hydrophilic properties.

3.4 Measurement

FT-IR spectra in the range of 400-4000 cm-1 were used to determine the functional groups of PVA/CS nanofiber (thermo scientific nicolet 8700 FT-IR spectrometer). The nanofiber surface morphology was studied after gold coating using a Scanning Electron Microscope (SEM, LEO 435VP). Image processing software was used to measure the nanoparticle diameter from the SEM micrographs. The specific surface area determined using Brunauer–Emmert–Teller method (BET, Sorptometer 1042). Heavy metals concentration in the sample solution was determined by an atomic adsorption spectroscope (Varian atomic adsorption 240).

3.4.1 Swelling Test

In order to investigate the stability of Chitosan/PVA nanofibers in an aqueous solution, 10 mm×10 mm pieces of Chitosan/PVA nanofiber membranes was immersed in 250 ml of deionized water at 30 ˚C for 24 h before and after heating cross-linking. The swelling percentage was calculated by:

$$\text{Swelling (\%)} = [(W_w - W_d)/W_d] \times 100 \quad (1)$$

where W_w and W_d were the masses of the swollen and dried nanofiber membranes, respectively.

4 Result and Discussion

4.1 Development of Regression Model Equation

The experiment was done according to runes sheet that reported in Table 2 with responses data.

Table 2: The factors Coded in experiments design

No	Run	Coded level				Responses	
		X_1	X_2	X_3	X_4	Y_1	Y_2
1	17	-1	-1	-1	-1	325	0.032
2	20	1	-1	-1	-1	327	0.038
3	30	-1	1	-1	-1	345	0.037
4	2	1	1	-1	-1	358	0.041
5	8	-1	-1	1	-1	344	0.034
6	15	1	-1	1	-1	365	0.039
7	3	-1	1	1	-1	351	0.045
8	19	1	1	1	-1	370	0.048
9	22	-1	-1	-1	1	345	0.03
10	11	1	-1	-1	1	352	0.036
11	14	-1	1	-1	1	364	0.035
12	10	1	1	-1	1	370	0.04
13	27	-1	-1	1	1	345	0.032
14	25	1	-1	1	1	372	0.037
15	5	-1	1	1	1	352	0.043
16	23	1	1	1	1	410	0.046
17	12	-2	0	0	0	320	0.04
18	9	2	0	0	0	420	0.051
19	4	0	-2	0	0	301	0.03
20	16	0	2	0	0	440	0.049
21	29	0	0	-2	0	432	0.037
22	28	0	0	2	0	450	0.039
23	21	0	0	0	-2	310	0.041
24	26	0	0	0	2	320	0.031
25	6	0	0	0	0	486	0.049
26	24	0	0	0	0	486	0.049
27	13	0	0	0	0	486	0.049
28	18	0	0	0	0	486	0.049
29	1	0	0	0	0	486	0.049
30	7	0	0	0	0	486	0.049

For both responses Y_1 and Y_2 and nanofiber weight, respectively, quadratic model was selected as suggested by the software. The final empirical models in terms of coded factors after excluding the insignificant terms for swelling (%) (Y_1) and nanofiber weight (Y_2) are as follows:

$$Y_1=+486+14.71X_1+17.62X_2+6.62X_3+6.04X_4+2.44X_1X_2+2.69X_1X_4-1.94X_2X_3+1.19X_2X_4-1.69X_3X_4-31.91X_1^2-31.91X_2^2-14.28X_3^2-45.78X_4^2 \qquad (2)$$

$$Y_2=+0.0493+0.0025X_1+0.004X_2+0.0016X_3-0.015X_4-0.0004X_1X_2-0.0003X_1X_3+0.0001X_1X_4+0.0001X_2X_4-0.0001X_3X_4-0.0012X_1^2-0.0027X_2^2-0.0031X_3^2-0.0036X_4^2 \qquad (3)$$

The adequacy of the models was stayed by analysis of variance (ANOVA). For swelling (%) and nanofiber weight responses in Eq. (2) and Eq. (3), the model F-value of 15.64 and 29.05 implies the model is significant for Y_1 and Y_2, respectively. There is only a 0.01% chance that an F-value this large could due to noise. P-values less than 0.0500 indicate model terms are significant. In Y_1 case X_1, X_2, X_1^2, X_2^2, X_3^2 and X_4^2 are significant model terms. And in Y_2 case X_1, X_2, X_3, X_4, X_1^2, X_2^2, X_3^2, X_4^2 and X_2X_3 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

4.2 The Effect of the Polymer Solution Concentration

The polymer solution concentration effect on the Swelling (%) of nanofiber, according to Fig. 2, increasing the concentration of Cs/PVA polymeric solution improves the stability of nanofibres, Of course, with an increase of more than 6 and 10 (wt%) for the Cs and PVA solution, respectively, it led to a decrease in the electrospanning speed and also a greater potential difference was needed. This is shown in Fig. 3 so that the amount of nanofibers produced in one hour was increasing with Concentrate the polymer solution.

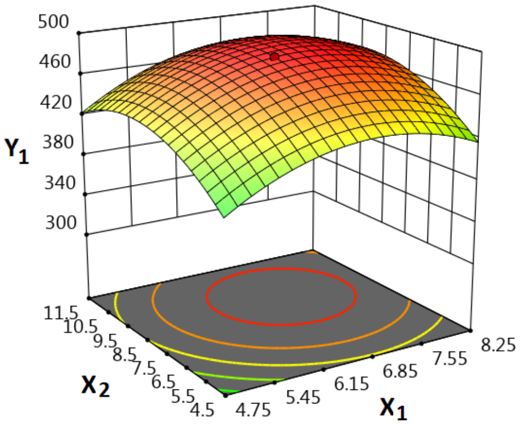


Fig. 2 The combined effect of Cs (X_1) and PVA (X_2) solution concentration on the Swelling (%) of Cs/PVA nanofiber.

The results showed that in dilute polymer solutions, electrospinning was performed at a voltage of less than 14 KV and with a greater distance (16 cm), because in this case the strength of the electric field caused the polymer solution of syringe needle to not be discharged into fibers, but was thrown as a drop.

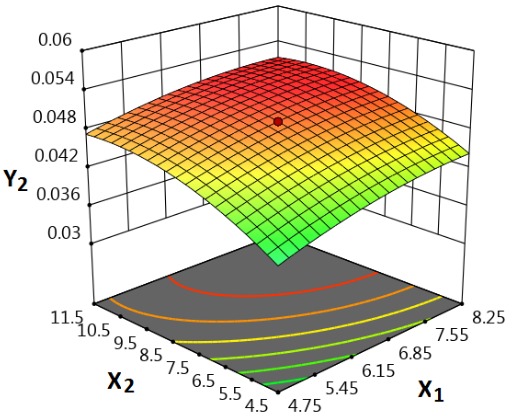


Fig. 3 The combined effect of Cs (X_1) and PVA (X_2) solution concentration on the Cs/PVA nanofiber weight that produced in 1 h.

4.3 The Effect of Cross-Linking Temperature

Nanofibers made of Cs and PVA in a suitable combination under different temperatures for cross-linking were investigated (Fig. 4). The results showed no crosslinking at temperatures below 100 °C, also at temperatures above 112 °C, it appears that the polymeric structure of nanofibers is degraded and the nanofibers stability decreases in water.

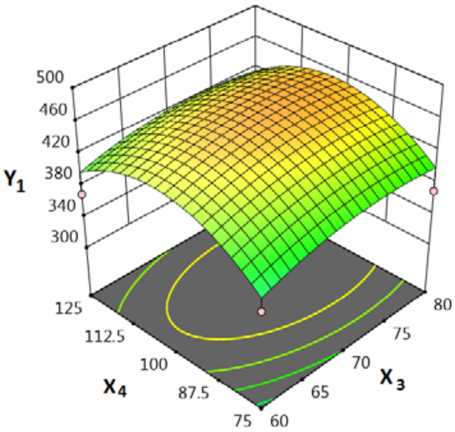
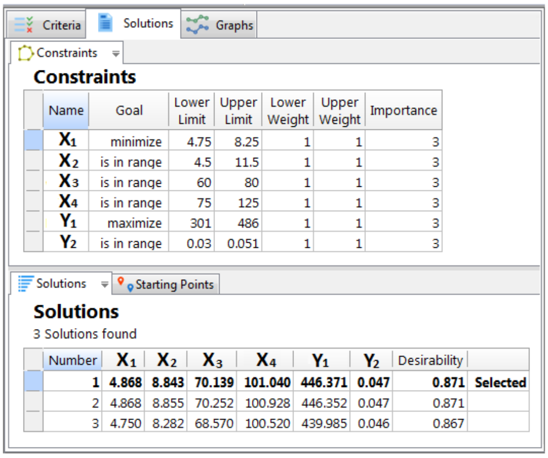


Fig. 4 The combined effect of Cs percentage (V/V%) (X_3) and cross-linking temperature (X_4) on the Swelling (%) of Cs/PVA nanofiber.

4.4 Optimization

According to results of experiments obtained optimum condition for production of Cs/PVA nanofiber. The Design Expert 11.0 software purposed 3 solution for our aim that shown in Fig. 5.

In this study maximum Swelling (%) for stability of nanofiber was important goal, also easily of electrospanning operation was important goal that was dependent to polymers solution concentration. So we select 5 and 9 (wt%) of concentration for Cs and PVA solution, respectively. Cs:PVA ratio was selected 7:3 and 100 °C was better temperature for cross-linked of Cs/PVA nanofiber.



Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
X_1	minimize	4.75	8.25	1	1	3
X_2	is in range	4.5	11.5	1	1	3
X_3	is in range	60	80	1	1	3
X_4	is in range	75	125	1	1	3
Y_1	maximize	301	486	1	1	3
Y_2	is in range	0.03	0.051	1	1	3

Solutions

3 Solutions found

Number	X_1	X_2	X_3	X_4	Y_1	Y_2	Desirability	
1	**4.868**	**8.843**	**70.139**	**101.040**	**446.371**	**0.047**	**0.871**	**Selected**
2	4.868	8.855	70.252	100.928	446.352	0.047	0.871	
3	4.750	8.282	68.570	100.520	439.985	0.046	0.867	

Fig. 5 The solutions of optimum condition for experiment goal.

4.5. Characterization of Nanofiber

As shown in Fig. 6, the functional groups were characterized by FT-IR spectrometer. In PVA/Chitosan nanofiber membrane, a broad bond at 3200-3550 cm^{-1} was assigned to O-H from the intermolecular and intramolecular hydrogen bonds. The peaks at 1383 cm^{-1} and 1467 cm^{-1} were assigned to the CH_3 symmetrical deformation mode. The C-H group peaks were observed at 1340 and 1370 cm^{-1}. The vibrational band observed between 2850 and 3000 cm^{-1} refers to the stretching C-H from alkyl groups. The absorption broad bonds at 985 and 1020 cm^{-1} were assigned to C-O stretching vibration Chitosan. The C-H group vibration peaks were observed at 1230 and 1323 cm^{-1}. The absorption bonds around 3462 cm^{-1} were assigned to N-H stretching vibration. Absorption bands in the range of 1545-1560 cm^{-1} were assigned to the primary amino groups. The SEM image of Chitosan/PVA electrospun nanofiber membrane has been shown in Fig. 3. As shown, the homogeneous nanofibers were produced at a voltage of 18 kV, with a tip-collector distance of 14.5 cm and flow rate of 0.5 ml/h. cross-linking of Chitosan/PVA electrospun nanofiber was also observed. Furthermore, Fig. 7 shows the different diameter frequencies of nanofibers according to SEM images using the image processing software. Therefore, the average diameter of nanofibers is 99.47 nm.

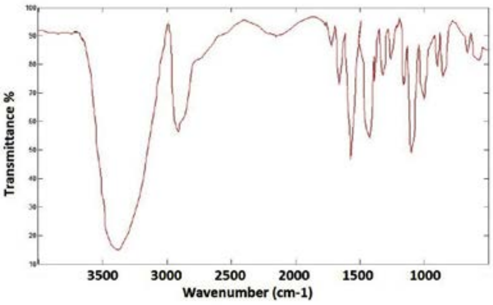


Fig. 6 FT-IR spectra of PVA, chitosan and chitosan/PVA nanofiber membranes.

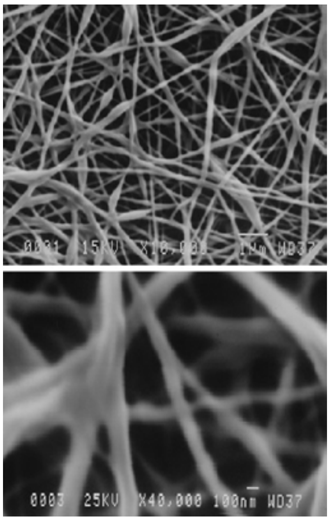


Fig. 7 The SEM image and diameter distribution of chitosan/PVA nanofiber membranes.

5 Conclusion

Cs/PVA nanofiber membranes were made by electrospinning process. The dilution or thickening of the polymeric solution disrupts the electrospinning process. Using direct heat, cross-linking were created in the Cs/PVA nanofiber without the use of chemicals.

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