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Using Chitosan as a Thickener for Electrospinning Dilute PVA Solutions to Improve Fibre Uniformity

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Abstract

Chitosan was added to PVA aqueous solutions as a thickener to improve the electrospinning process. The presence of a small amount of chitosan considerably improved the uniformity of as-spun nanofibres. This improvement is attributed to its significant effect on the solution viscosity and conductivity, with only a slight impact on the surface tension. The concentration of the PVA required to produce bead-free and uniform nanofibres was reduced with the increase in chitosan concentration. The chitosan thickener suppressed the jet break-up and facilitated the jet stretching so that fine and uniform fibres could be electrospun even from a dilute PVA solution.

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1. Introduction

Electrospinning can produce polymeric nanofibres for diverse applications in biomedical engineering[1, 2], filtration[3-5], protective clothing[6], catalysis reaction[7], chemical sensors[8, 9] and nano-composites[10-12]. It typically involves a solution spinning process, in which the polymer solution driven by a strong electric field is quickly stretched into dry or semi-dry filaments and directly deposited on the collector, usually in the form of non-woven fibre mats. An improved electrospinning process is able to create oriented nanofibre arrays[13-15] or to produce multi-component nanofibres, such as core-sheath nanofibres [16, 17] and side-by-side bicomponent nanofibres[18].

The electrospinning process and the resultant fibre morphology are dependent on the operating parameters (e.g. applied voltage, flow rate and collecting distance) and material properties (e.g. the type of polymer, molecular weight, solvent used, polymer concentration, viscosity, conductivity, and surface tension)[19, 20]. For a given polymer-solvent system, the polymer concentration plays a major role in determining the fibre morphology because it affects other solution properties such as viscosity, conductivity and surface tension. Although finer fibres can be electrospun by reducing the polymer concentration, beads or beaded fibres are usually formed. Uniform fibres cannot be obtained unless the polymer coils are highly entangled in solution, which requires a polymer concentration far larger than its "overlap concentration"[21].

To stop the formation of beads, ionic additives, such as salts[22], surfactants[23] and polyelectrolytes[24], have been used. The addition of these additives effectively increases the solution conductivity and the net charge density[25]. Beads are reduced or eliminated due to the increase in fibre stretching. However, these ionic additives are not always effective. When the polymer concentration is low, beads are constantly generated even if ionic additives are present in the solution[26].

Thickener, a polymer showing high viscosity in dilute solution, has been used widely in industry as a rheology modifier to improve processability or product performance. The addition of a small amount of thickener to a solution could significantly increase the solution viscosity, but does not alter the solution functionality. However, it is not yet established if the use of a small amount of a thickener can modify the solution properties sufficiently so that fine and uniform fibres can be electrospun.

Chitosan is a linear polysaccharide consisting of β-1, 4 linked 2-amino-2-deoxy-D-glucopyranose. It has been used as a thickener in the food industry[27]. At acidic pH, chitosan behaves like a linear cationic polyelectrolyte and shows high charge density because of the protonation of its amino function groups[28, 29]. Due to its high viscosity in dilute aqueous solution and good compatibility with many water soluble polymers such as poly(vinyl alcohol)(PVA)[30, 31], poly(ethylene oxide)(PEO)[32] and poly(vinyl pyrrolidone)(PVP)[33], chitosan is particularly suitable for use as a thickener to improve the rheological properties of an aqueous polymer solution for electrospinning. Electrospinning of chitosan blended with a water-soluble polymer, such as PVA[34], PEO[35] and silk fibroin[36], has been found to improve the fibre fineness. However, the use of chitosan as a thickener for improving the nanofibre uniformity, especially for electrospinning a dilute polymer solution, has not been reported.

In this paper, we used chitosan and PVA as model compounds to demonstrate the concept of using chitosan as a thickener to improve the fibre uniformity in electrospinning. We have found that the addition of 1% wt chitosan to a dilute PVA solution is able to electrospin bead-free, uniform and fine nanofibres, even when the PVA concentration is very close to its overlap concentration.

2. Experimental details

Materials and instrument

PVA (M_w 146, 000-186, 000, 98-99% hydrolysed), chitosan (low molecular weight, 75~85% deacetylated) and acetic acid were obtained from Aldrich and used as received. All polymer solutions were made using deionised water. As chitosan is only soluble in acidic aqueous solution, 2% (wt) of aqueous acetic acid solution was used as a solvent for making the PVA/chitosan solutions. In order to eliminate the effect of acetic acid on the electrospinning process, the same solvent was also used to prepare the PVA solution. The PVA/chitosan solutions were prepared by dissolving PVA in a dilute aqueous chitosan solution containing 2% acetic acid at 80^OC.

The solution viscosity and conductivity were measured with a digital rotational viscometer (D443 Rheology International) and a conductivity meter (LF330 Merck), respectively. This viscometer has a 5% experimental error and good sensitivity. The surface tension was determined by the Du Nouy Ring method, using a platinum ring (Cole Parmer) and a precision electronic balance (AEA 160 DA ADAM). The fibre morphology was observed under a scanning electron microscope (SEM, LEO1530 microscope). The average fibre diameter and bead density were calculated from the SEM pictures with the aid of a computer software (Image*Pro* plus 4.5).

Electrospinning

A purpose-built electrospinning apparatus[23] was used for this work. A polymer solution was put into a plastic syringe and connected through a metal syringe needle (20 Gauge) to a high DC voltage power supply (ES30P, from Gamma High Voltage Research). A grounded aluminum sheet, 15cm away from the tip of the syringe needle, was used to collect the as-spun fibres. The flow rate of the PVA solution was controlled by a syringe pump (KD Scientific). All electrospinning processes were conducted at 22kV of applied voltage with the flow rate in 0.6ml/hr.

3. Results and discussion

Electrospinning an aqueous PVA solution could result in individual beads, beaded-fibres or uniform fibres, depending on the PVA concentration. Koski et al[37] indicated that a fibrous structure could be electrospun when the concentration was beyond C[η] ~4, where [η] is the intrinsic viscosity and C is the PVA concentration. C[η] ~4 corresponds to the overlap concentration of polymer, above which the polymer motion will be dominated by the presence of direct polymer-polymer interactions and coil entanglement[38]. However, if the PVA concentration C[η] exceeds 10, a pseudo matrix-gel will be formed.

Based on the molecular weight value and the Mark-Houwink relation[39], the intrinsic viscosity of the PVA used can be estimated as:

$$[\eta] = 6.51 \times 10^{-4} M_w^{0.628} \qquad (1)$$

The concentration of PVA corresponding to C[η]4~10 should be in the range of 3.25~8.14% (wt). Although our experiment has confirmed that fibrous products were produced when the PVA concentration was in the range of 4~8% (wt), beads-on-string structures were formed for the whole concentration range. The addition of 2% acetic acid to these PVA solutions slightly improved the fibre morphology, but the as-spun fibres still had a beads-on-string fibre morphology (**Figure 1**).

The addition of a small amount of chitosan in these PVA solutions led to a considerable change in the fibre morphology. Non-beaded and uniform fibres were electrospun from 7wt% and 8wt% PVA solutions when they contained 0.5 wt % chitosan. Though beaded-fibres still resulted from more dilute PVA solutions (4~6%), the bead number decreased apparently. Higher concentrations of chitosan in PVA solutions would further improve the fibre uniformity. As shown in **Figure 2**, when the PVA solutions contained 1% chitosan, uniform fibres were produced from solutions with a PVA concentration in the range of 5~8wt% and beaded fibres appeared only when the concentration was below 4wt%. It is reasonable to expect that higher chitosan concentration in PVA solution would lead to further improvement in the fibre uniformity.

From the SEM images, the bead density and the average fibre diameter of as-spun nanofibres can be calculated. The bead density, the number of perceived beads in every 100 micron square of sample, can be used to characterize the beads generated in electrospun fibre mats. The dependence of the bead density on the PVA concentration is shown in **Figure 3a**. Larger bead density occurred when lower concentrations of PVA solutions were electrospun, and the bead density value decreased as the PVA concentration increased for all studied electrospinning PVA systems. However, the addition of chitosan to PVA solution affected the bead density considerably. When there was no chitosan in the solution, the bead density varied from 62 to 5 (per 100 μm^2) when the PVA concentration was increased from 4wt% to 8wt%. However, the addition of 0.5wt% chitosan to the PVA solutions reduced the bead density to 43 for 4wt% PVA solution, and the density value was very close to zero when the PVA concentration was larger than 7wt%. The addition of 1wt% chitosan to the PVA solution resulted in lower bead density values; the bead density was 22 for the 4% PVA solution, while the value became zero for other higher PVA concentrations in the solutions.

Like other electrospinning polymer systems, the average fibre diameter increased with an increase in the PVA concentration. The relationship between average fibre diameter and PVA concentrations is shown in **Figure 3b**. When compared to those from the chitosan-containing PVA solution, the fibres electrospun from the PVA-only solutions, containing acetic acid, had a lower average fibre diameter, although they had a beads-on-string structure. The average fibre diameter increased with an increase in the chitosan concentration. This can be attributed to a higher overall polymer concentration of the chitosan-containing PVA solutions and the better fibre uniformity of the as-spun fibres.

As the electrospinning process was conducted under the same operating conditions and using the same polymer system, the fibre morphology changes should be derived from the effect of chitosan on the solution properties. As shown in **Figure 4a**, the solution viscosity increased with an increase in the PVA concentration and this was observed for all the PVA solution systems. The addition of chitosan to the PVA solution increased the

solution viscosity. At the same PVA concentration, the viscosity increased with an increase in the concentration of chitosan. However, the increase in viscosity was not linear with the concentration of chitosan. The viscosity increase for a PVA solution having higher PVA concentration was larger than that in a solution having a lower PVA concentration. For example, the viscosity of a 6wt% PVA solution was 299cP. When the solution contained 0.5wt% chitosan, the viscosity was 506cP, an increase of 69%. But when the solution contained 1 wt% chitosan, the solution viscosity increased to 917cP, a further increase of 81%.

The effects of PVA concentrations and chitosan on the surface tension are shown in **Figure 4b**. As the PVA concentration increases, the surface tension increases slightly. Such a slight increase in surface tension with PVA concentration could be attributed to the existence of acetic acid increasing the ionic interaction in the polymer solution[40]. The addition of chitosan to the PVA solution also leads to a slight increase in the surface tension. However, the variation of the surface tension due to the addition of chitosan was within 2 dyn/cm. In contrast to the viscosity change, this difference is very small.

The solution conductivity shows a linear dependence on the PVA concentration. As shown in **Figure 4c**, the solution conductivity increased with an increase in the PVA concentration. Even for the PVA solution without any acetic acid and chitosan, the solution conductivity increased by about 30% when the PVA concentration increased from 4wt% to 8wt%. A similar result was also found in a previous study[41], and the reason has been attributed to a hydrogen-bond network forming in the PVA solution. With the addition of acetic acid to the PVA solution, the solution conductivity increased due to the existence of acetate ions and higher concentration of free hydrogen proton. Further addition of chitosan to the PVA solution increased the solution conductivity significantly. Larger increases in the conductivity were observed in solutions having a lower PVA concentration. When the solution contained 1% chitosan, the solutions with PVA concentration in the range 5~8wt% had very high conductivity and the conductivity was little influenced by the PVA concentration. Only 4% PVA solution was found to result in a slight decrease in the conductivity.

During the electrospinning process, the charged jet interacts with the external electrical field, and charge induced repulsion occurs within the jet. The jet undergoes a bending instability[42], also called "whipping instability"[43, 44], and stretches into fine filaments. Under the action of surface tension, the jet tends to minimise its surface area. The capability for a jet to maintain its uniform fibre morphology is highly dependent on the viscosity. If the fluid has low viscosity, the jet cannot maintain its fibrous structure, thus breaking up into interconnected sections. These sections can then further split into smaller sections and tend towards a spherical shape, while the inter-connected parts are stretched into ultra-fine filaments. As a result, a beads-on-string structure forms. With an increase in viscosity, the jet break-up will be suppressed, thus reducing the bead number and increasing the fibre diameter. When the viscosity is larger than a critical value, the jet overcomes the surface tension to form uniform filaments.

High solution viscosity reflects strong polymer-polymer interaction occurring in the solution. Polymer-polymer interaction within the PVA solutions comes from polymer coil entanglement and hydrogen-bond interaction. As the PVA concentration is larger than the overlap concentration, coil entanglement and hydrogen bond interaction among the PVA macromolecules should take place. However, the formation of beaded fibres suggests that the entanglement and polymer-polymer interaction are not sufficient to maintain uniform fibre morphology. The increase in the solution viscosity due to the addition of chitosan indicates an enhancement in the polymer-polymer interaction due to extra chitosan polymer coils and their hydrogen-bond interaction with PVA macromolecules. High solution viscosity and strong polymer interaction between chitosan and PVA considerably suppress the effect of the surface tension, thus resulting in uniform fibres.

In acetic acid solution, the amino groups of chitosan react with acetic acid forming ammonium cationic ions. Charge repulsion causes the chitosan chains to expand in the solution and further enhances the interaction between PVA and chitosan. The multi-ionic characteristic and the strong interactions would make the two polymers associate with an ionic complex[45]. With such high solution conductivity, the solution has a high net charge

density[25]. Jet and filaments would be stretched under stronger forces. The bead could be eliminated due to this enhanced stretching process, and also fibre diameter would tend to reduce, just like the case with the addition of ionic surfactant[23].

All these effects on the solution properties tend to result in finer and more uniform fibres. The 7wt% PVA solution containing 0.5wt% chitosan was able to produce uniform fibres about 220nm in diameter. Finer and more uniform fibres were electrospun from 5wt% PVA solution containing 1wt% chitosan, with a diameter of 160±38nm. Other researchers have confirmed[34] that the finer fibres can be further electrospun if the PVA solution contains a higher concentration of chitosan.

4. Conclusion

This study has shown that using a cationic polyelectrolyte chitosan as a thickener for electrospinning aqueous PVA solution can effectively improve fibre uniformity and reduce fibre diameter. Non-beaded and uniform fibres can be electrospun from PVA solution of a low concentration that usually produces beaded fibres in the absence of a suitable thickener. The improvement in the fibre uniformity due to the addition of chitosan is attributed to increased solution viscosity and conductivity, because the chitosan functions like a thickener and an ionic additive. At high solution viscosity, the jet break-up is effectively suppressed and the increased solution charge density enhances the fibre stretching. As a result, uniform nanofibres can be electrospun even if the solution concentration is close to its "overlap concentration".

It is expected that this concept will be suitable for electrospinning other polymer systems. Uniform and fine nanofibres will be produced if the polymer solution is augmented with a small amount of compatible thickener, which is able to improve both the solution viscosity and conductivity, yet have little effect on the solution surface tension.

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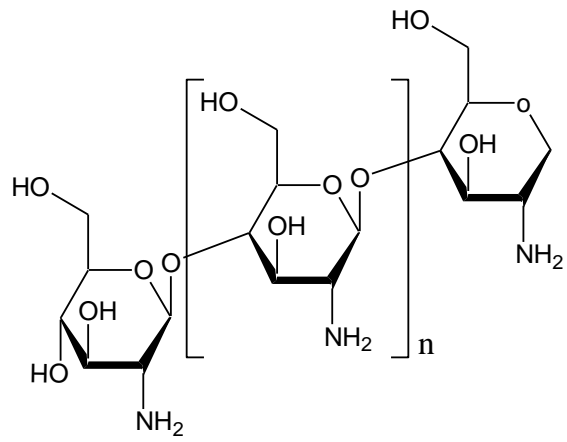[45]   Aoi, K, Takasu Aand Okada M 1995 *Macromolecular Rapid Communications* **16** 757-61
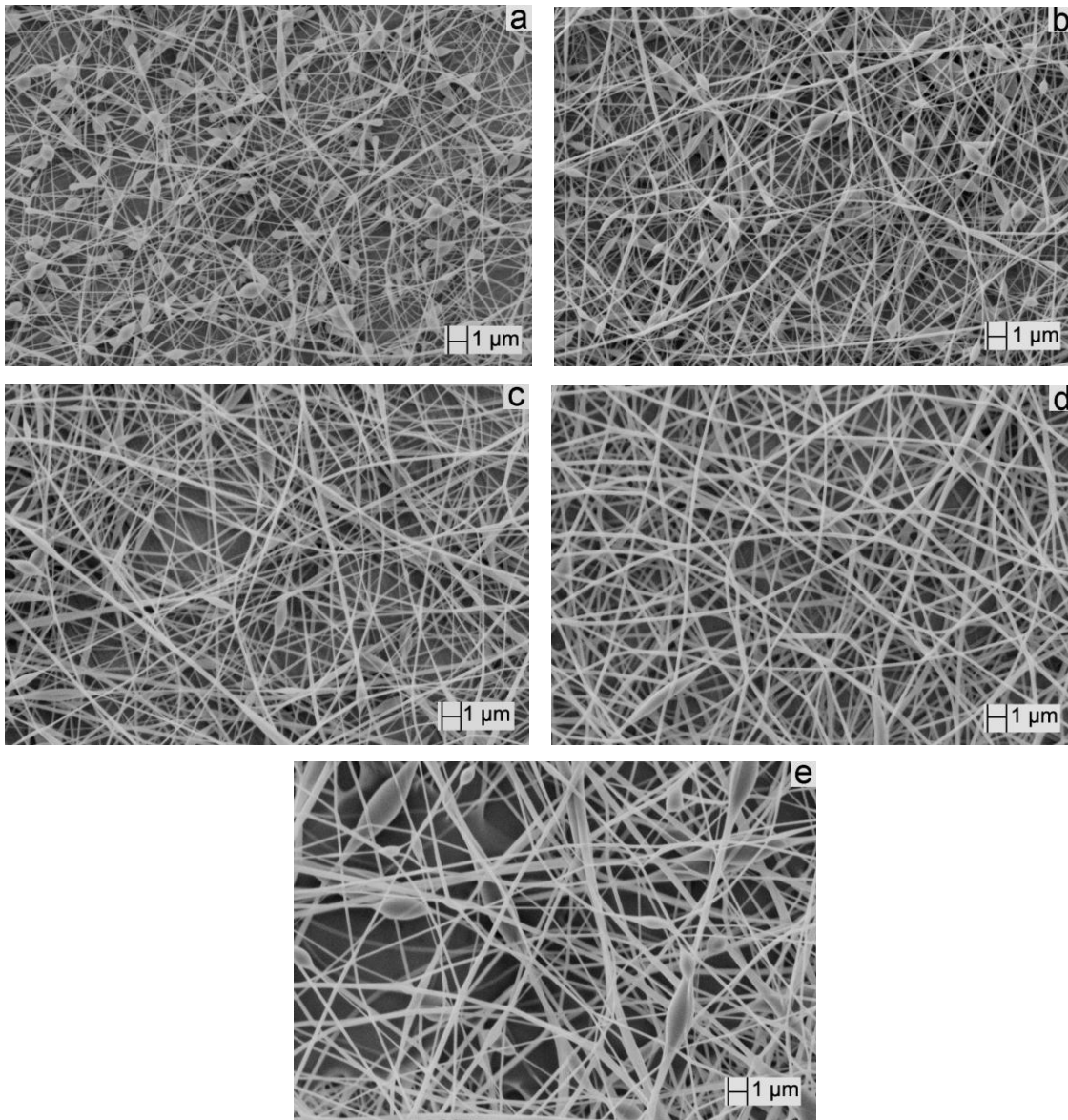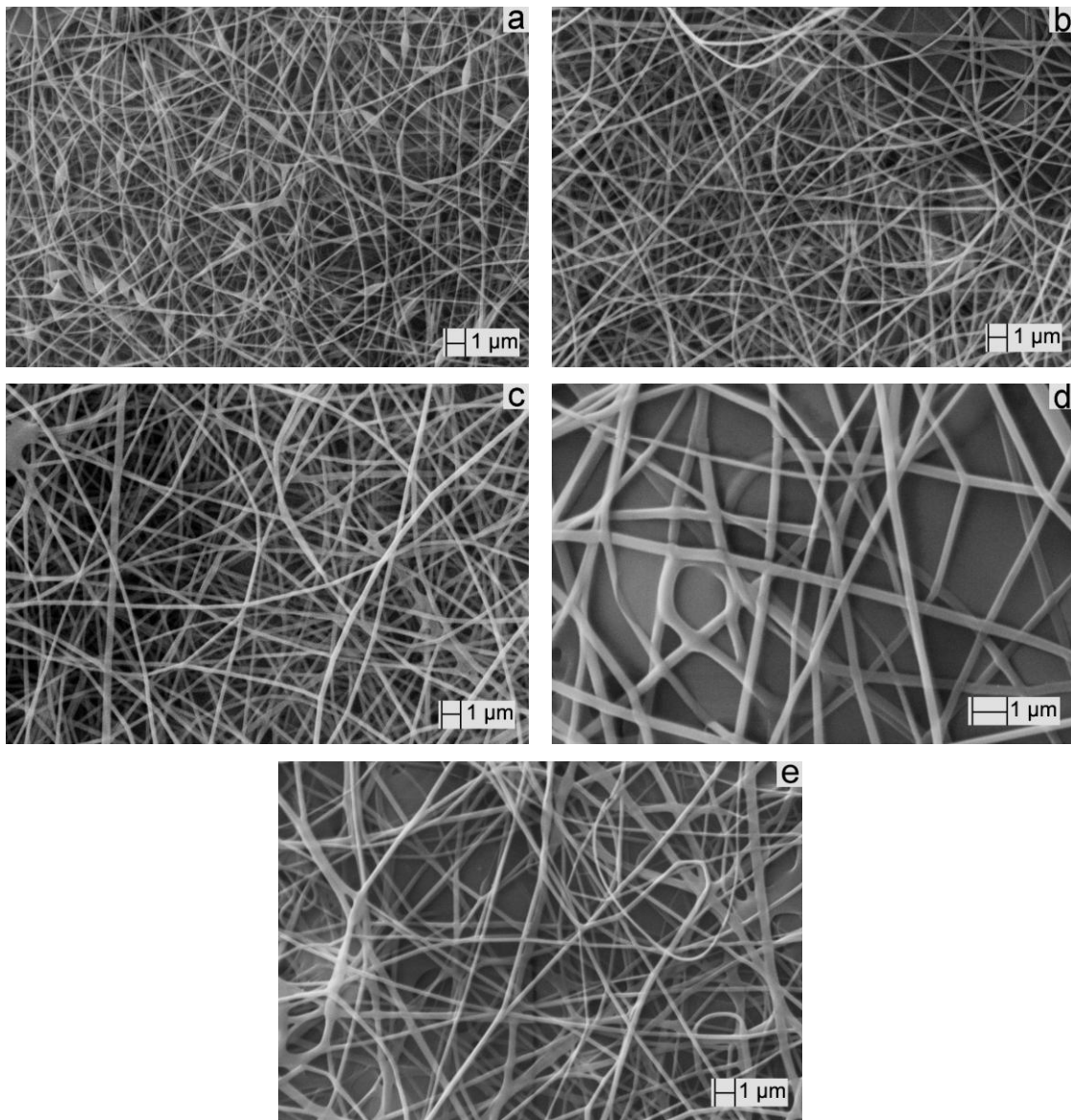
Figure 1: SEM images of PVA nanofibres electrospun from PVA solution containing 2% acetic acid, PVA concentration (a) 4wt%, (b) 5wt% (c) 6wt% (d) 7wt% (e) 8wt%.

Figure 2: SEM images of PVA nanofibres electrospun from PVA solution containing 1% chitosan and 2% acetic acid, PVA concentration (a) 4wt%, (b) 5wt% (c) 6wt% (d) 7wt% (e) 8wt%.

Figure 3: Dependence of bead density and average fibre diameter on the PVA concentration. Symbol (*) indicates the formation of uniform electrospun fibres.

Figure 4: Dependence of solution viscosity, conductivity, and surface tension on PVA concentrations. The standard deviations are included in the brackets.

(Chitosan)

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PVA 8wt%

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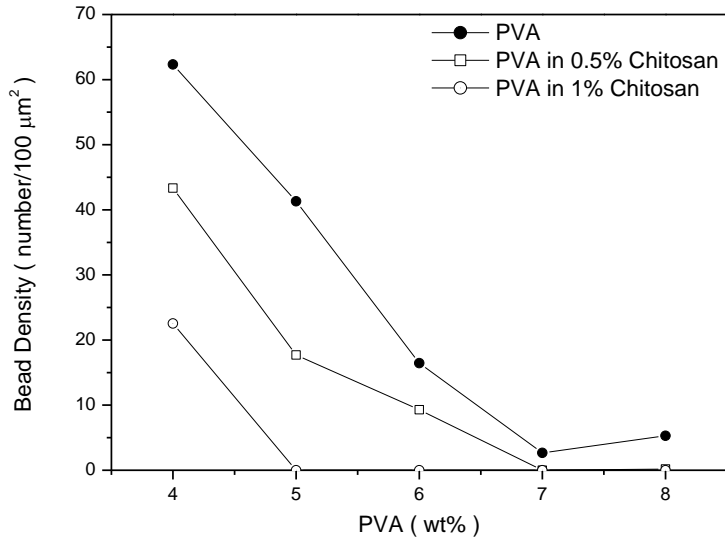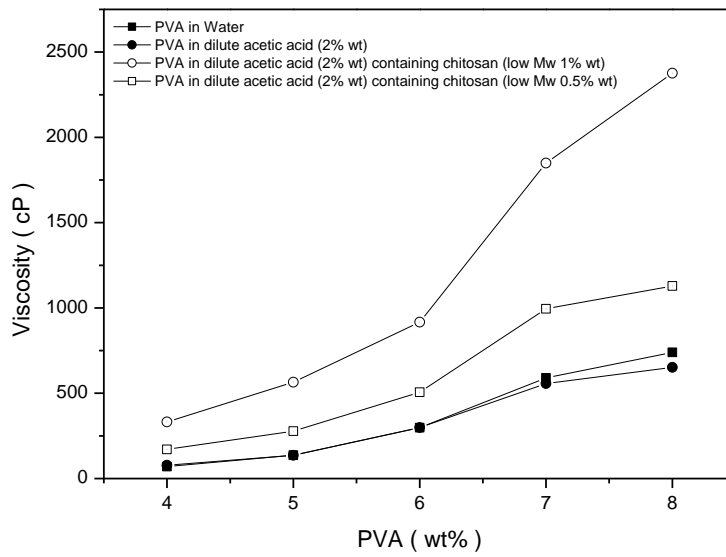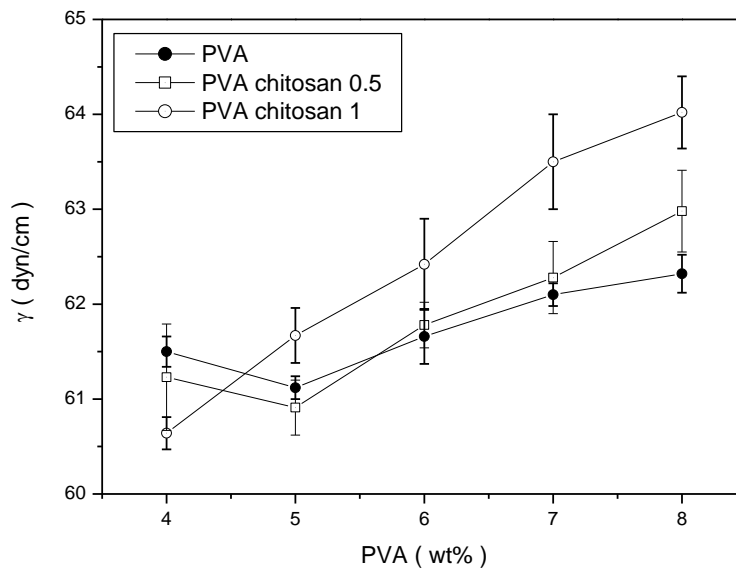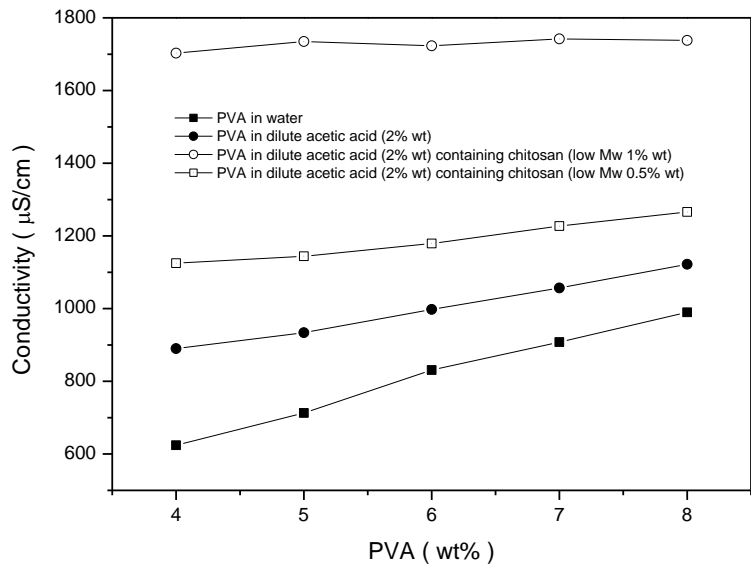
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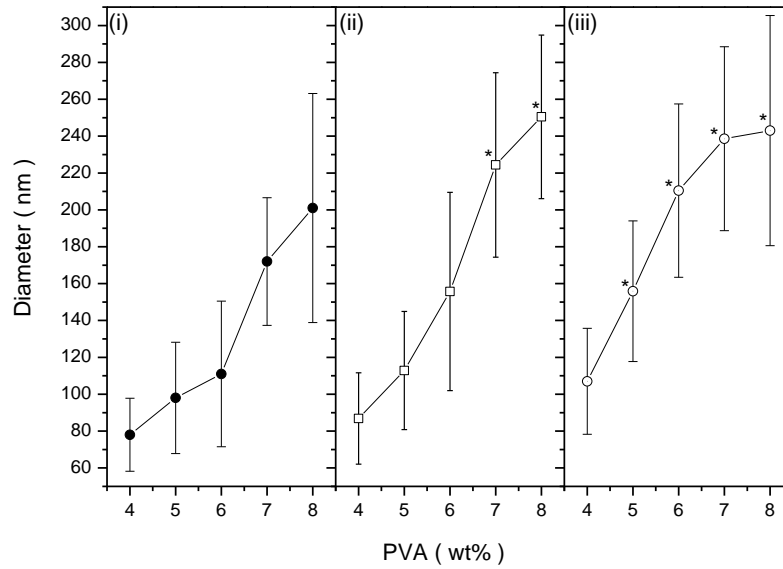
(3b)

Figure 3: Dependence of bead density and average fibre diameter on the PVA concentration. Symbol (*) indicates the formation of uniform electrospun fibres.

(4a)

(4b)

(4c)

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