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Electrospun Fibrous Mat of Cellulose Acetate: Influence of Solvent System (Acetic Acid/Acetone) on Fibers Morphology

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ABSTRACT

Objectives: Electrospun Cellulose Acetate (CA) fibers system are of high demand due to its desired properties associated with the final fiber features. This polymer inability to dissolve may hinder its electrospinning processing. The goal of the current study is to explore the fiber forming ability of solvent mixture of varying ratios of acetone and acetic acid and to derive the optimized formulation that facilitate the continuous and uniform CA fiber formation. **Methods:** In this study, a new solvent system for electrospinning of cellulose acetate is developed for the preparation of continuous uniform CA fibers. Different concentrations of cellulose acetate are dissolved in solvent system consisting of acetic acid/acetone mixture. The polymer solution prepared was hosted in a mechanical syringe pump, with a stainless-steel blunt end needle fixated to the tip acting as the spraying nozzle. The polymeric cellulose acetate in acetone/acetic acid mixture was examined for its viscosity and electrical conductance. Moreover, the formed cellulose acetate-based fibers were morphologically examined. **Results:** The solvent system composition as well as the cellulose acetate concentration affected the final CA fiber morphology, where the 10% cellulose acetate solution in acetone: acetic acid at 9:1 ratio presented uniform fiber morphology with a diameter of 549±45 nm. The solvent system optimized preserved continuous and uniform, beads-free CA fibers. **Conclusion:** In the current study, the different solvent systems studied presented different fiber morphologies and diameter sizes thus preserving the importance of the solvent system for the cellulose acetate fine fiber production.

Key words: Acetic acid, Acetone, Cellulose acetate, Electrospinning, Fibers.

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INTRODUCTION

Electrospinning, a term derived from electrostatic spinning which fundamental idea dates to more than 60 years ago. It serves to provide experimental production of polymer filament presenting a longstanding importance in many fields of pharmaceutical application.[1] The fabrication of the fibers depends on the presence of the opposite charged polarities, where the polymer solution bears a different charge than the collector area. Once the electrically charged polymer solution is dispensed from the needle spinneret, the solvent evaporates thus producing fibers on the collector.[2] The parameters affecting the final fibers characteristics include both process and formulation variables. Formulation parameters are exemplified by the type of polymer and its concentration and the solvent system which should be suitable for the polymer, while the process variables devised for the production of the required mats include the distance between the spinneret and the collector, the voltage applied and the solution flow rate.[3]

Various polymers have been utilized for pharmaceutical application such as polyethylene oxide,[4] chitosan,[5] alginate,[6] polyvinyl acetate[7] as well as cellulose acetate. CA is a derivative of cellulose and possesses the ability to be processed into films, membranes and ultra-fine fibers.[8] However, utilization of cellulose acetate as a fibrous building unit is a real challenge as it presents a limited solubility properties. Furthermore the ability of this polymer to be spun into fine fibers depends highly on process and formulation parameters.[9]

Fabrication of cellulose acetate-based fibers necessitates the use of different concentrations and solvent systems for the production of fine mats. Solvents at different ratios were employed for CA fiber formulation include dioxane, pyridine, dimethylacetamide (DMAC), acetic acid, dimethylformamide (DMF) yet these solvent studied present a major limitation due to their toxic property.[8,10,11]

The goal of the current study is to explore the fiber forming ability of solvent mixture of varying ratios of acetone and acetic acid and for deriving the optimized formulation that facilitate the continuous and uniform CA fiber formation.

MATERIAL AND METHOD

Material

Cellulose acetate CA (MW=50,000), acetic acid (>99%) and acetone was purchased from sigma Aldrich (Steinheim, Switzerland). Acetic acid and acetone were mixed by volume, for example the mixed solvent system containing acetone/acetic acid at a ratio of 9:1(v/v%) is abbreviated to acetone/acetic acid (9:1).

Preparation of the cellulose acetate solutions and electrospinning process

Spinning solutions consisting of a mixed solvent systems were prepared at room temperature 25 ±0.5°C, the systems prepared by dissolving cellulose acetate at various solvent ratios ranging from 9:1 to 1:9 acetone:acetic acid with appropriate CA amount required to prepare 5, 10 and 15% w/v concentration.

Each of the solution prepared was hosted in a mechanical syringe pump, with a stainless-steel blunt end needle fixated to the tip (24 gauge) acting as the spraying nozzle. A high voltage DC power supply was used to generate the potential difference across the needle and the stainless-steel

collector, with the emitting positive polarity electrode attached to the needle and the negative potential electrode connected to the collector. The syringe pump incorporating the solution was set at a constant flow rate of 1.5 ml/hr at a tip to collector distance of 15 cm. The electrospinning formulations were performed in a Plexiglas box at constant relative humidity of 30±1% and temperature of 25 ± 0.5°C.

Fiber morphological observation

The morphological appearance and diameters of the formed fibers from the electrospun formulations were examined by the Scanning Electron Microscope (SEM) (SERON technology, AIS2300C, Korea). The samples fabricated were placed on a double adhesive tape and using a cressington sputter coater 10801, gold coated at pressure less than 0.1 mbar and 20 mA current, the samples were scanned at different magnifications. The scanned fiber samples obtained were analyzed using image J program over 50 points in order to obtain its average diameter.[12]

Viscosity and conductance determination of the electrospun solution

The spinning solutions were characterized using rotational rheometer (ARG2 TA, Crawley, West Sussex) to determine their rheological characteristics utilizing 50 mm diameter cone-plate geometry. Polymer solutions were calibrated thermally at 25±0.5°C within the testing equipment. Furthermore, the conductance of tested mixtures were measured with conductometry at 25± 0.5°C. The significance differences between the results was tested using ANOVA where probability p value <0.05 indicates significance.

RESULTS

Cellulose is considered as a renewable polymer source, its acetate derivative is used to fabricate films and fibers. This polymer recently has attracted attention as an electrospun fiber forming polymer for its known thermal stability and chemical resistance properties. Yet, the production of the cellulose actetate fiber is determined by its solubility in a solvent system with suitable characteristics for electrospinning process.[11]

Three concentrations of the polymer were studied with varying solvent mixture ratios. Fiber morphology and fiber/bead diameters obtained were investigated to determine the optimal polymer concentration and solvent system composition.

The influence of concentration and the solvent mixture composition are prominent for fiber morphology where the increase in CA concentration transferred the product morphology from beaded-fibers to a uniform filament fiber (Table 1). The electrospinning of 5% CA solution in 1:9 acetone/acetic acid solvent mixture yielded only irregular beads while upon increasing concentration to 10%, fibrous beads are formed as presented by Figure 1 (A).

As presented in Table 1, using a ratio of 3:7 acetone/acetic acid solvent mixture, different concentrations yielded various fiber morphologies. At 5% CA concentration, beaded fibers are observed the morphology of the fiber is improved upon increasing the concentration to 10% resulting in a decrease in beads and enhancement in fiber structure, this concentration represented the minimal concentration suitable for polymer chain entanglement. Another sign that can illustrate the effect of the polymer concentration is the size of beads present in the formed fibers for example, at same acetone/acetic acid solvent ratio the beads have scaled down from 7.324±1.8 µm with 5% to 3.749±1.63 µm with 10% polymer concentration. Further increase in CA concentration to 15% didn't form any fibers on the collector.

The different solvent mixtures studied were able to maintain the ability to dissolve the CA at various concentrations and to perform continuous electrospinning. Each solvent systems affected the fiber formation differently which was demonstrated by the morphological variation. At 5% polymer concentration, beads were solely obtained at 1:9 all through 5:5 acetone/acetic acid ratio while at 7:3 ratio, beaded fibers started to evolve. While, the polymer concentration 10% dissolved in solvent system ratio between 1:9 and 5:5 resulted in beaded fibers as demonstrated in Figure 1 (A, B and C) which transformed into ribbon and uniform fibers at ratios above 7:3 acetone/acetic acid as shown in Figure 1 (D and E). Furthermore, the solvent system influence on the fiber morphology can be depicted by the increase in acetone relative concentration from 30 to 50% v/v resulted in a decrease in the bead size from 3.749±1.63 µm to 1.615±0.99 µm (Figure 1).

Effect of polymeric solution viscosity and conductance

At 10% polymer concentration which is the lowest value capable of forming fibers, the viscosity of the solvent mixture increased with increasing the acetic acid concentration as demonstrated in Figure 2. The increase in viscosity is obtained upon acetic acid percentage growth; the rough increase was seen by shifting the ratio of acetic acid above 30% beyond this concentration the increase leveled off (Figure 2). Optimal viscosity for fiber formation was presented at less than 30% acetic acid at 2.24 pa.

The study reveals that the decrease in viscosity from ratio 7:3 to 9:1 affected the average diameter as demonstrated in Table 1, where the diameter decreased with the decrease in viscosity (0.883± 0.0811 µm to 0. 549± 0.21 µm).

The second solvent mixture factor includes, the conductance where the presence of the acetic acid alone conserves minimal conductance with respect to acetone, as it sustains a good conductance equivalent to 53 µsec/cm, which can support the establishment of fiber formation. The solvent mixture shows an exponential increase in the conductance upon addition of acetone to the acetic acid. This phenomenon led to enhance the conductance, which is reflected on the fibers morphology. Figure (3) demonstrates the increase in conductance with the increase in acetone content, this reflects to a decrease in number of beads until reaching an optimal conductance where beads-free fiber with acceptable diameter is obtained (Table 1).

DISCUSSION

Reports indicated the ability of cellulose acetate to dissolve in numerous solvent systems which affected the final fiber morphology and diameter.[8,10,11] This highlights the effect of the solvent system on the fiber forming ability of CA and fibers characteristics. With the obstacle of continuous electrospun CA fibers and the suitability of the solvent, different mixtures evaluated for continuous fiber formation such as dioxane, acetone, DMF, DMAC: acetic acid, DMAC: acetone, acetic acid.[8,9] Although fibers were formed using DMF and DMAC solvents but one shouldn't neglect the toxicity of these solvent which may remain in traces within the fiber formed.[13]

As a consequence for these limitations, researchers have adapted acetic acid as a dissolution medium for CA which is a decent solvent for this cellulose derivative, despite the dominant use of acetic acid as a main solvent for electrospinning of CA, it demonstrated short fibers with high bead count, this is explained by the weak electrospinning properties of acetic acid.[8] In our study, this problem was subdued through the inclusion of acetone as a secondary solvent to enhance the electrospinning features of acetic acid. In order to determine the optimal concentration of CA, 5%, 10% and 15% (w/v) polymer content was utilized in various solvent mixtures.

In order to tackle the assumption of single solvent system ability to form CA fibers, the use of individual solvents was evaluated. The use of acetic acid solely presented highly beaded mats with minimal fiber formation independent on polymer concentration. Whilst, the use of acetone as a solo solvent resulted in fine fibers, but a critical problem arouses due to

Table 1: Composition and characteristic of polymeric CA electrospun fiber.

Acetone/ Acetic acid % (v/v)	% CA (w/v)	Fiber morphology	Fiber diameter (µm)	Beads diameter (µm)
1/9	5%	Beads only	N/A*	10.932±3.22
	10%	Beads only	N/A	7.018±1.8
3/7	5%	Bead only	N/A	7.324±1.534
	10%	Beaded fiber	N/A	3.749 ± 1.63
5:5	5%	Beads only	N/A	5.83 ±1.46
	10%	Beaded fibers	N/A	1.615± 0.99
7/3	5%	Beaded fibers	N/A	2.645 ± 1.2
	10%	Fibers and Ribbons	0.883± 0.0811 2.986±1.12	N/A
9/1	5%	Few beads	N/A	1.86 ±1.47
	10%	Fibers	0.549± 0.210	N/A

* N/A (not applicable)

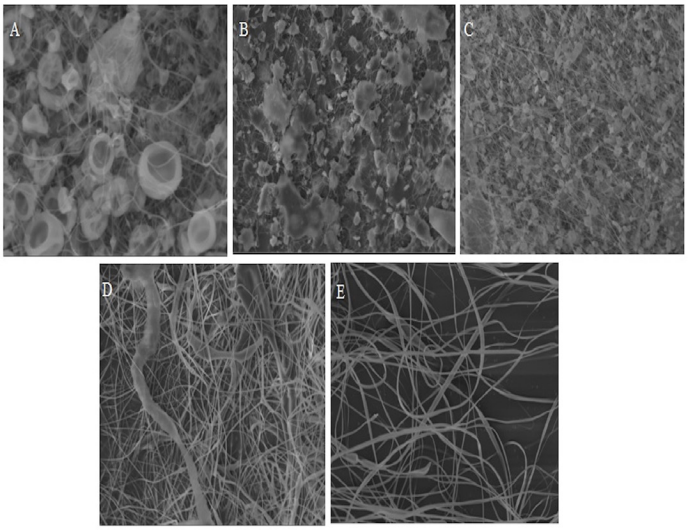
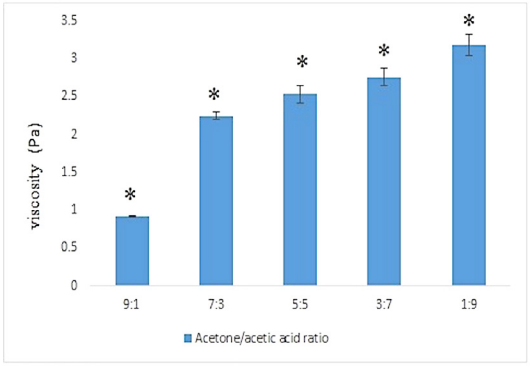


Figure 1: Scanning electron micrographs of cellulose acetate of 10% CA electrospun fibers prepared in different acetone/acetic acid at ratio of (A) 1:9; (B) 3:7; (C) 5:5; (D) 7:3; (E) 9:1.

rapid evaporation of acetone during the electrospinning which required high flow rate of a minimum 10 ml/hr to prevent clogging of the needle. The high flow rate wasn't the only limitation as the rapid flow rate led to increase the yield loss to about 50%. The effects of using only one solvent presented ultimate drawbacks, thus, the utilization of acetone/acetic acid mixture was assessed.

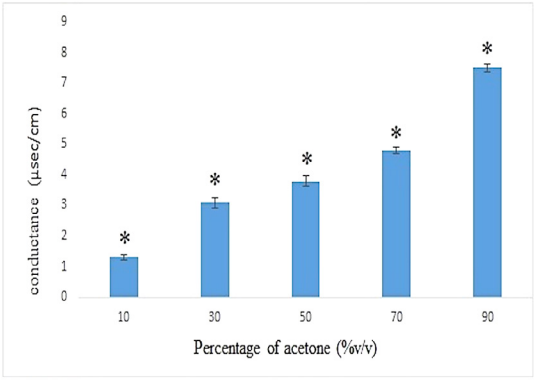
In a study by Han *et al.* the CA was dissolved in acetic acid/water solvent system at a CA concentration minimal of 17% for fiber formation. Due to the change in the solvent system in the current study different concentrations of CA were performed at each solvent mixture to optimize the concentration range of CA.

As presented in Table 1, CA concentration controlled the formed fiber morphology. The effect of the polymer concentration is reflected by fiber formation, diameter, uniformity and presence of beads. This is explained by the chain entanglement of the liquid ejected allowing fibers to be formed upon solvent evaporation thus decreasing the beads size.[11] Further increase in CA concentration to 15% didn't form any fibers on



*p value<0.05

Figure 2: The viscosity of cellulose acetate polymer in various solvent mixtures.



*p value<0.05

Figure 3: The alteration of conductance with respect to different solvent mixtures.

the collector due to high viscosity of the polymer solution, which led to formation of heavy droplets which were lost prior to electrospinning as well as clogging of the spinneret.

The concentration of the polymer wasn't the only factor affecting the fiber morphology, where at a specific concentration different fiber morphology was observed with fluctuating the solvent system. Each solvent systems affected the fiber formation differently which was demonstrated by the morphological variation as seen by Figure 1. This is explained by the effect of the solvent properties, where the acetic acid presents a slow evaporation as its boiling point is 117.9°C while that of acetone doesn't exceed 56.9°C allowing fast evaporation of acetone which gives rise to local phase separation while the slow evaporation of acetic acid preserves a solvent rich regions which are presented as pores during the electrospinning process as presented in Figure 1A.[11] The improved fiber formation is attributed to higher vaporization efficacy of acetone with respect to acetic acid which allows rapid evaporation.[10]

The transformation from beaded fibers to bead free ribbons and fibers at higher concentration in certain solvent mixture is due to the polymer chain entanglement in the solution which allows essential continuity of the electrospinning process for uniformity to occur.

Effect of polymeric solution viscosity and conductance

The morphological transformation of the cellulose acetate polymer solution into continuous CA fiber is dependent on the solvent system as well as CA concentration that reflects the influence of both polymeric solution viscosity and conductance. The increase in viscosity at higher content of acetic acid may be associated with the expansion of the CA chains in the presence of acetic acid.[10] Interestingly, the average fiber diameter

was affected by the conductance of the solvent mixture.[14,15] Where the conductance is significant for the fiber formation since electrospinning depends on charge transfer for the fabrication of fibers, thus the conductance of the solvent is essential for optimal fiber formation.[16]

CONCLUSION

Electrospun beaded fibers; ribbon-like fibers and uniform fibers were obtained upon varying the acetic acid/acetone binary solvent ratios and polymer concentration. Varying morphologies affected by the polymer concentration and the final binary system ratios were investigated. The two main factors that were prominent are the polymer concentration and the acetone ratio with respect to the acetic acid. Precisely at 10% CA concentration and above 70% acetone ratio, the ribbon and fiber free of beads were created. In this study, the different solvent system studied presented different morphologies and diameter sizes thus preserving the importance of the solvent system for the CA fine fiber production.

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CONFLICT OF INTEREST

The author declares no conflict of interest.

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