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Influence of Triton X-100 on PVA Fibres Production by the Electrospinning Technique

Abstract

Electrospinning represents a low cost technique applied in the production of micro- and nano-fibres. The use of poly(vinyl alcohol) as supporting matrix in aqueous solution for fibre deposition introduces important advantages related with drug release (based on the low toxicity of polymer). On the other side, imperfections of resulting fibres (bead formation) represents an impediment to be circumvented. The introduction of non ionic surfactant (triton X-100) circumvents bead formation and improves the homogeneity of fibre, as verified in the analysis of thermal, structural and morphological properties of PVA net. The results indicate that minimal dispersion of triton X-100 in solution (in the order of 1 wt%) affects the circularity of beads, while at 10 wt% a reduction in the defect concentration in the order of five times is verified with a reasonable reduction in the diameter of the remaining defects and improvement in the regularity of fibres.

Key words: *electrospinning, poly(vinyl alcohol) fibres, surfactant, beads, fibre production.*

Introduction

Electrospinning (electrostatic spinning) is an interesting technique developed by Formhals (1934 - 1940) [1 - 3] based on the production of micro- and nano-fibres using an electrostatic force. Increasing interest in the study of electrospinning has been evident in literature when considering potential applications of electrospun fibres in materials science and biotechnology [4 - 8] and in the development of structures that can be progressively applied as prototypes for drug delivery and tissue scaffolds [9, 10].

Different polymers (poly(vinyl alcohol), poly(vinyl pyrrolidone), poly(vinylidine fluoride)hexafluoropropylene, poly-(ethylene glycol) and chitosan) [11, 12] and dispersions of nanoparticles in polymer solution are conveniently applied in the deposition of regular fibres [9, 13] from the pumping of material through a spinneret.

If a strong electric field is applied on the drop, a process of charge separation is established with competition between the surface tension and electrostatic force. While surface tension gives a spherical shape to the droplet, the electrostatic force tends to deform it, according a Taylor's cone [14 - 16], which is located around the droplet of polymer at the needle tip. The ejection of a charged cone-jet is established since the electrostatic repulsion between ions and their attraction in the direction of the grounded target (collector) increases until the limit in which it overcomes the surface tension.

Optimization of the polymeric template can be considered one of the most important parameters in the performance of eletrospun fibres. In this sense, poly(vinyl alcohol)-PVA - a conventional polymer produced by polymerisation (and subsequent hydrolysis) of vinyl acetate monomer [17] represents a potential candidate when considering low toxicity and high solubility in water [18]. Nanofibres of PVA prepared via electrospinning [19, 20] have been progressively used as templates for fuel cell systems [21], soft electronic materials [22], catalytic devices [23], radiation detection [24] and in filtration applications [25]. On the other hand, the inclusion of metal and semiconductor nanoparticles promotes a reasonable increase in the number of applications based on antibacterial action [26]. Additives such as titanium dioxide [27] and gelatin introduce advantages in the controlled release of drugs [28].

In spite of these important applications, the presence of defects in the structure of a net [20] (such as beads) is a result of the capillary breakup of the spinning jet provoked by inadequate control of the viscoelasticity, charge density or surface tension of the solution [29]. Consequently high flow rates of polymer bring out an inadequate drying process [30].
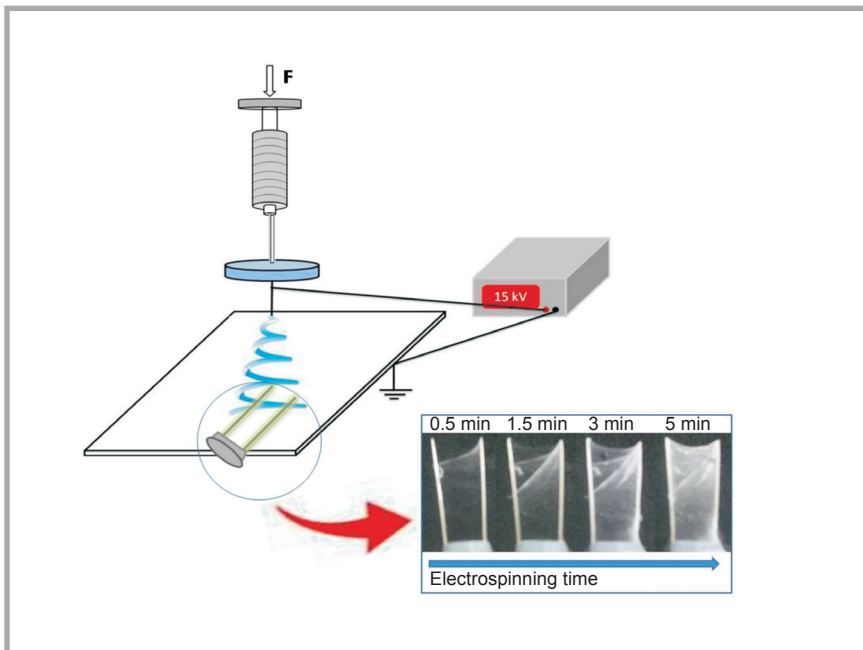
As reported in the literature, the control of bead formation results in the improvement of the elasticity of fibres [31], which is a function of the relative concentration of additives in the polymer solution. In this sense, the presence of surfactant introduces superior quality viz. a high surface per volume ratio, good porosity and the preparation of 1-D structures with an elevated degree of orientation [32]. In spite of this possibility, it has been reported that the process of bead formation is still unknown [29].

Another procedure applied in the minimisation of defects is based on the inclusion of a non-ionic surfactant which improves the regularity and reduces bead sizes and fraction, with the production of defect-free fibres and improvement in the yield of fibres as a consequence of surfactant inclusion in the polymer solution [33, 34].

Li Yao et al. [35] reported the correlation between the contact angle and the onset of electrospinning as a consequence of a decrease in the surface tension of the droplet induced by triton X-100. Wang et al. [36] reported the influence of glutaraldehyde (GA) in acetone on the crosslinking of PVA substrates and improvement in the water and mechanical resistance. In both papers, Triton X-100 was used in order to lower the surface tension and, consequently, to establish a regular feed rate of the polymeric solution. The typical concentration of TX-100 is in the range of 0.02 to 1.2 v/w% and 0.03 to 1.5 v/w% (respectively). Our paper presents a statistical study of the influence of Triton X-100 (in a broad range of concentration of 0.93 v/w% to 10.28 v/w%) on bead deposition. We explored the influence of surface tension, measured by the stalagmometric method, on the homogeneity of electrospun fibres.

Experimental

Poly(vivnyl alcohol) with typical average MW 85,000 - 124,000 99+% hydrolysed and triton X-100 (TX-100) were purchased from Aldrich (USA) and used as received. The polymer content in aqueous solution (50 ml) was 8 wt% and the dispersion was established in a thermal bath during 3 hours at 80 °C. The surface tension was measured at

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Figure 1. *Experimental setup of electrospun system and as–spun fibres collected on the sample holder as a function of time.*
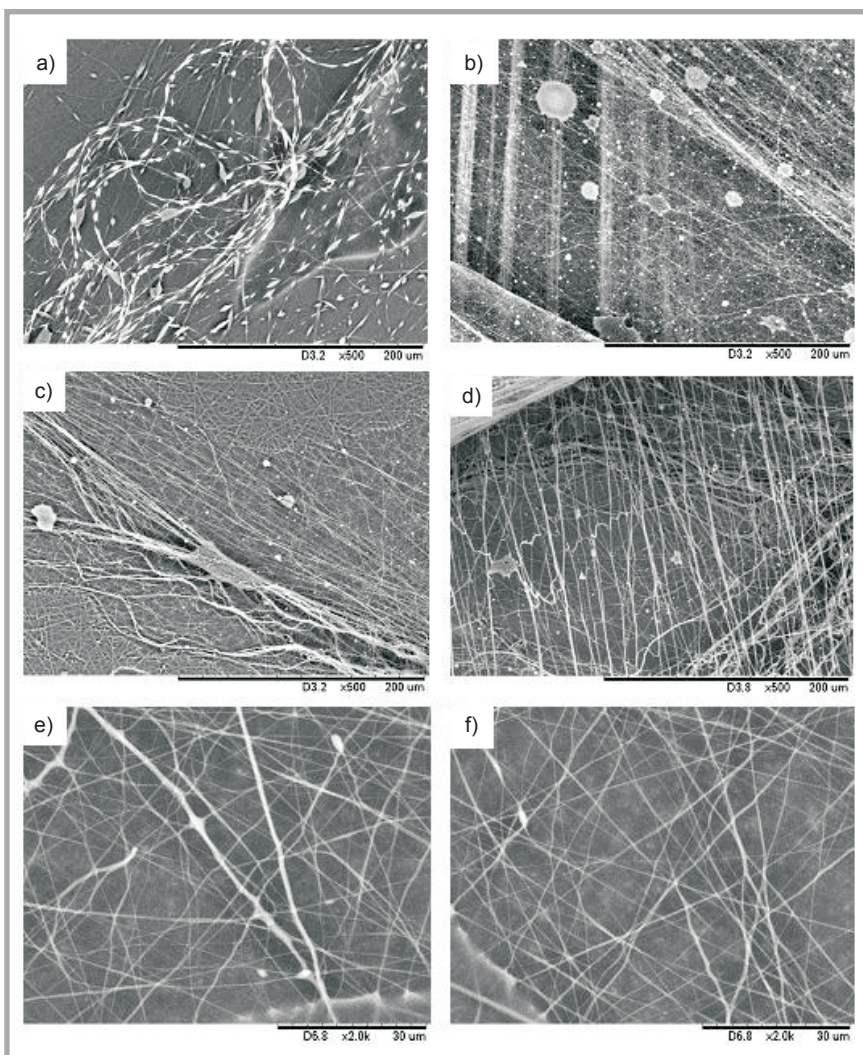
Figure 2. *SEM micrographs of electrospun fibres at different TX-100 concentrations (wt%): (a) 0, (b) 1, (c) 2, (d) 5, (e) 8 & (f) 11. All electrospinning processes were carried out at room temperature in a vertical spinning configuration with a deposition time of 5 minutes.*

20 °C using the stalagmometric method. Variable amounts viz. 0v/w%, 0.93 v/w% (1 wt%), 1.87 v/w% (2 wt%), 4.67 v/w% (5 wt%), 7.48 v/w% (8 wt%) and 10.28 v/w % (11 wt%) of triton X-100 were added to the polymer solution. After that the mixture was put in a syringe maintained at a fixed pressure with a flux of 166 µl min^{-1} without an external electric field. With a regular flux of polymer solution established in the direction of the target, a voltage in the order of 15 kV was applied between the tip of the spinneret and the grounded target.

The experiments were conducted with progressive deposition of fibres on the surface of a collector at a fixed time (five minutes) and an analysis was performed with the use of images of SEM at the same magnification (600 ×).

The sample holder was placed on the surface of the grounded target plane as described in **Figure 1**. On the surface of the electrodes, two parallel metal needles were used as collectors, from which the net was deposited.

The distance between the capillary and collector is 10 cm, while the diameter of the needle is 0.7 mm. At each concentration of surfactant, 10 different images from SEM were obtained with an area per image of (328.6 × 246.4) µm^2.

The statistics of bead formation along the fibres were determined with the use of ImageJ software, a public-domain image processing and analysis program developed at U.S. National Institutes of Health (NIH), applied in biological analysis [37 - 41], from which the images were explored in order to quantify the number and average of the area of beads as a function of the surfactant amount. The images were obtained using a SEM Hitachi TM1000, while thermal properties were explored with the use of a differential scanning calorimeter - Shimadzu DSC-60. All pans were prepared with the insertion of 1 mg of each sample and the heat process was established at a scanning rate of 10 °C min^{-1} and N$_2$ flux of 50 mL min^{-1}.
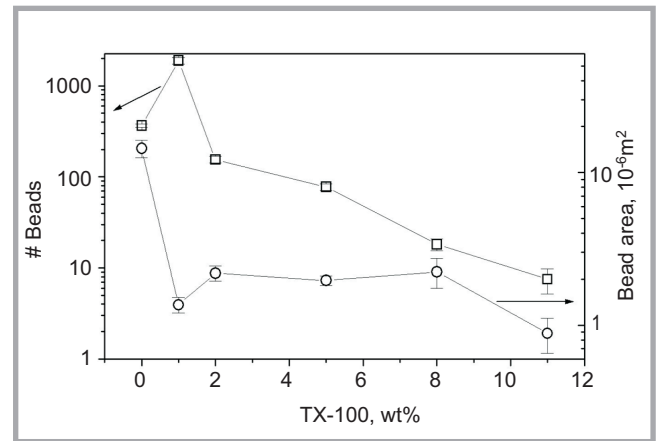
■ Results and discussion

At a fixed interval of time (5 minutes of deposition) the as-spun fibres collected on the surface of the sample holder were analysed under a SEM. As we can see in the images of **Figure 2**, the progressive inclusion of the surfactant (images *a* to *f*
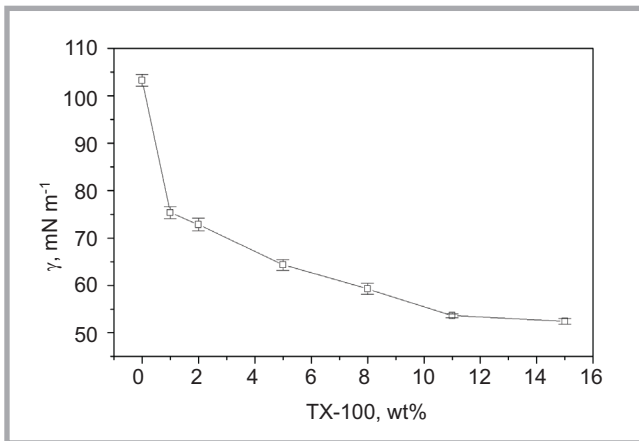
Figure 3. *Surface tension of PVA polymer solution as a function of the dispersed amount of TX-100.*

Figure 4. *Number of beads per image and relative area of beads as a function of the amount of TX-100 dispersed in aqueous solution.*

- with variation in the surfactant concentration from 0 wt% (0 v/w%) to 11 wt% (10.28 v/w%)) causes an apparent reduction in bead concentration with the production of more regular structures.

These results show the direct dependence on the surface tension of the polymer solution. As we can see in **Figure 3**, the surface tension decreases greatly with the progressive inclusion of TX-100 and a minimum is established at a concentration above 11 wt%.

The minimal variation verified at 11 wt% indicates that the negligible influence of the surfactant is detected with progressive inclusion of the surfactant in the polymer solution, as detected by the saturation point in the surface tension of droplets. It is important to remember that reduction in the surface tension strongly affects the competition established with an electrostatic force during electrodeposition.

Considering that a constant electric field is established at an increasing concentration of the surfactant, it is possible to infer the influence of the additive on the bead formation rate. The dependence of the number of defects on the amount of surfactant dispersed on the polymer solution is shown in **Figure 4**. The number of beads increases greatly at a low concentration of the surfactant (if compared with the absence of TX-100), while the bead area is reduced with progressive insertion of the surfactant.

The number of beads per image increases (7×), while the bead area is reduced (15×). In spite of the increase in the number of beads, it represents the starting point in which the bead disper-

sion process is established, considering that particles in the structure of fibres are reduced in diameter in comparison with neat PVA microfibres. The progressive inclusion of TX-100 into the solution reduces both the number and area of beads and homogeneous structures are obtained with a reduction in the number of defects. Note that the bead fraction (as shown in **Figure 5**) is greatly reduced (five orders), indicating that the regularity of fibres produced is significantly enhanced.

It is important to verify in this curve (**Figure 5**) the direct relationship between the surface tension and surfactant amount and the direct implication on bead formation. The influence of surfactant inclu-

sion on the regularity of fibres is summarised in **Table 1**.

An interesting aspect to be considered from **Table 1** is that the circularity degree of beads is strongly affected by the presence of surfactant dispersed in the polymer solution. In spite of the slight dependence of the degree of circularity on the concentration of surfactant, the major role established by the amount of TX-100 is verified in the size and number of defects distributed along the fibres. Compared to the thermal characterisation of fibres, it is known that a reduction in the melting temperature is associated with the crystalline state of fibres due to the rapid solidification of fibres during

**Figure 5.** *3-D map of bead fraction as a function of the surface tension and TX-100 concentration.*
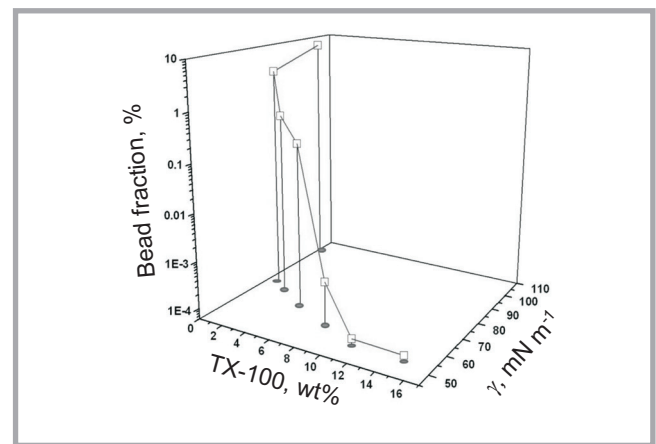
Table 1. *Influence of the surfactant on surface tension and beads properties.*

TX-100, wt%	γ, mN m^{-1}	Number of beads	Bead area, μm^2	Bead fraction, %	Circularity (0 - 1)
0	103.3 ± 1.3	365.3 ± 15.2	14.39 ± 0.79	6.43 ± 0.36	0.47 ± 0.02
1	75.4 ± 1.2	1894.1 ± 152.8	1.36 ± 0.06	3.16 ± 0.30	0.89 ± 0.03
2	72.8 ± 1.3	154.8 ± 13.1	2.19 ± 0.19	0.42 ± 0.03	0.90 ± 0.01
5	64.3 ± 1.1	77.7 ± 6.5	1.96 ± 0.06	0.19 ± 0.02	0.94 ± 0.08
8	59.3 ± 1.2	18.2 ± 2.7	2.23 ± 0.20	0.0005 ± 0.0001	0.76 ± 0.05
11	53.6 ± 0.4	7.5 ± 2.3	0.88 ± 0.11	0.00008 ± 0.00001	0.97 ± 0.07
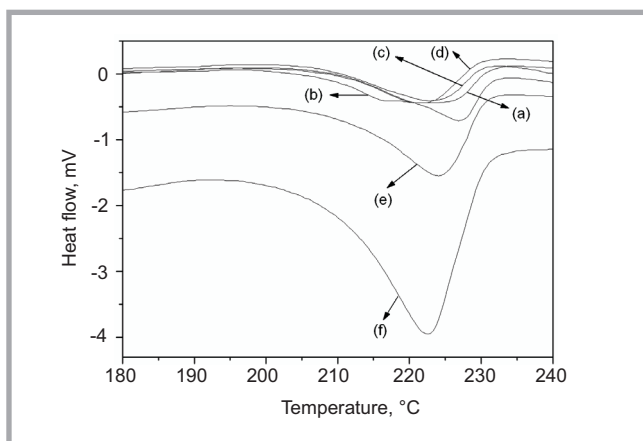
Figure 6. *Thermogram of PVA nanofibres at different concentrations of TX-100 (wt%): (a) 0, (b) 1, (c) 2, (d) 5, (e) 8 & (f) 11.*
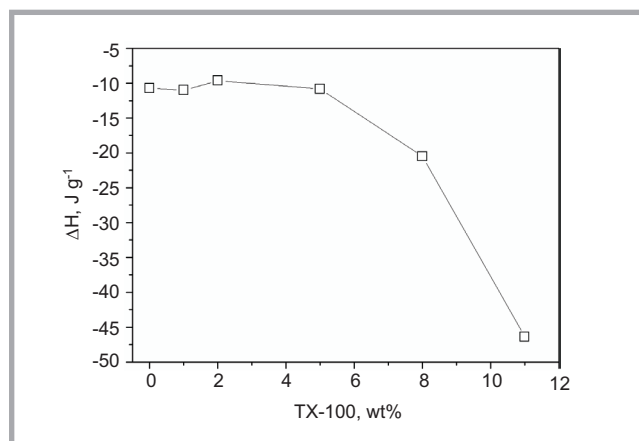
Figure 7. *Enthalpy of fusion of fibres as a function of TX-100 concentration.*

electrospinning. The results indicate that the superior properties of synthesised fibres (compared with neat PVA) preserve the melting point of PVA, typically identified as a sharp endothermic peak that remains at around 222 °C, as reported in the literature [42, 43]. The progressive inclusion of TX-100 during the synthesis slightly affects the critical temperature at which melting is established, as can be seen in *Figure 6*. In spite of this aspect, the enthalpy of fusion is strongly dependent on the surfactant amount dispersed in the polymer solution. The ΔH value increases (in modulus) with the progressive inclusion of the surfactant (as shown in *Figure 7*), indicating that regular and superior crystalline structures are obtained with a reduction in bead concentration. It is important to observe that the homogeneity of fibres is accomplished by elevating the crystalline degree of the synthesised material, indicating that superior properties are obtained from interaction between TX-100 and PVA during the electrodeposition.

■ Conclusions

We have shown that improvement in fibres can be successfully obtained from interaction between PVA and triton X-100. The increase in the amount of TX-100 dispersed in polymer solution (PVA aqueous solution) improves the spinnability and provides the production of fibres with superior quality and increasing crystalline properties. The optimal concentration of the surfactant is verified at the minimal value of surface tension of the polymer solution (concentration of TX-100 in the order of 10 wt%), from which negligible variation in the surface tension is detected with increasing

enthalpy of fusion of electrospun fibres. The optimisation of the TX-100 concentration applied in the PVA aqueous solution introduces important aspects in the development of specific applications, such as wound dressings and sun blocker, considering the regularity and control in the porosity of synthesised net.

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