

Cellulose

Ethyl Cellulose, Cellulose Acetate and Carboxymethyl Cellulose Microstructures Prepared using Electrohydrodynamics and Green Solvents

--Manuscript Draft--

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Corresponding Author:	Mohan Edirisinghe University College London Medical School London, UNITED KINGDOM	
Corresponding Author Secondary Information:		
Corresponding Author's Institution:	University College London Medical School	
Corresponding Author's Secondary Institution:		
First Author:	Maryam Crabbe-Mann	
First Author Secondary Information:		
Order of Authors:	Maryam Crabbe-Mann Dimitrios Tsaoulidis Maryam Parhizkar Mohan Edirisinghe	
Order of Authors Secondary Information:		
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Abstract:	<p>Cellulose derivatives (CD) are an attractive sustainable material used frequently in biomaterials, however their solubility in safe, green solvents is not widely exploited. In this work three cellulose derivatives; ethyl cellulose, cellulose acetate and carboxymethyl cellulose were subjected to electrohydrodynamic processing (EHD). All were processed with safe, environmentally friendly solvents; ethanol, acetone and water. Ethyl cellulose was electrospun and an interesting transitional region was identified. The morphological changes from particles with tails to thick fibres were charted from 17wt% to 25wt% solutions. The concentration and solvent composition of cellulose acetate (CA) solutions were then changed; increasing the concentration also increased fibre size. At 10wt% CA, with acetone only, fibres with heavy beading were produced. In an attempt to incorporate water in the binary solvent system to reduce the acetone content, 80:20 acetone/water solvent system was used. It was noted that for the same concentration of CA (10wt%), the beading was reduced. Finally, carboxymethyl cellulose (CMC) was electrospun with poly(ethylene oxide) (PEO), with the molecular weight and polymer compositions changed and the morphology observed.</p>	
Response to Reviewers:	<p>Response to Editor-in-Chief: Thank you for your comments. We appreciate you input and the suggestions you have made, we have made every effort to address them. I am willing to consider one further revision of this work. Besides the elevated misgivings of Reviewer #1 (a very distinguished cellulose scientist), I find that there are substantial language</p>	

problems that interfere with the understanding of the work. Also, the closing sentence of the abstract suggests that the diameter difference is not significant. That indicates poor analysis; what are we to imagine regarding less obvious places? I do not find that it is an especially worthwhile goal to replace cellulose in biomedical materials when cellulose is functional and can be chemically modified for specific purposes. Rather, the different morphologies that allow new applications would be meritorious. We have revised the document to address the language matter. We do not intend to replace cellulose, our argument was cellulose derivatives are easier to electrospin compared to cellulose. However, we have removed these statements as we do not want to prevent any confusion. Our aim is to highlight processing cellulose derivatives with safe solvents and produce a range of structures on order to encourage the use of all cellulose and these solvents.

Response to Reviewer 1:
Thank you for your review of our manuscript. We appreciate the detail you have presented and have made every effort to take these on board and address each point.

2. The frequent mentions about the difficulty of solubilizing cellulose and the connexion to the present study is confusing. The fact that this investigation dealt with three cellulose derivatives DOES NOT solve the problem of cellulose processing, simply because the three substrates are NOT cellulose itself. In other words, whereas the study is interesting, it does not deal with cellulose and hence it should be treated within its context without giving the idea that somehow it provides a means to solve the cellulose processing problems, because it does not. This study does not propose a solution to the solubility of cellulose. Instead, we wish to highlight the EHD processing of cellulose derivatives using safe solvents such as water, as this is not widely exploited. Electrospinning these derivatives with the solvents stated is very difficult. The volatile nature of ethanol and acetone make continuous production difficult. Water also poses problems with electrospinning, its high surface tension clash with the entire process, however, their non-toxic nature and availability outweigh these issues, pursuing this avenue of “green electrospinning” is important in terms of biomaterials and sustainability as a whole. We hope we have now made this clear in the revised manuscript.

4. The discussion of the results often lacks of depth and is therefore sometimes unconvincing, particularly in the case of CMC. The discussion in this work describe the morphologies produced via electrospinning the cellulose derivatives. Through changing various parameters different structures were produced and their fabrication was explained through established EHD principles. We have described in detail the procedures that have given rise to each of the different morphologies as we have changed parameters. We hope we have modified the text sufficiently while not losing form of our study as entitled it is a study of microstructures and we have made every effort to describe how they were prepared.

Re.: Submission of revised paper “Ethyl Cellulose, Cellulose Acetate and Carboxymethyl Cellulose Microstructures Prepared using Electrohydrodynamics and Green Solvents”.

Manuscript number CELS-D-17-00613.

Friday 19th January 2017

Dear Editor,

Thank you for your email dated 21/10/2017 enclosing the reviewers’ comments. We would like to thank the reviewer for their comments, they were critical but constructive, we appreciate the time they have taken to do this. We have carefully read the comments and have applied the appropriate revisions to the manuscripts. We have addressed each point individually below.

The changes in the manuscript have been highlighted in red.

We hope the revised manuscript now meets the standard required for Cellulose and we look forward to hearing from you.

Yours faithfully,

Prof. Mohan Edirisinghe

(Corresponding author)

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1 Ethyl Cellulose, Cellulose Acetate and Carboxymethyl Cellulose
2 Microstructures Prepared using Electrohydrodynamics and Green Solvents

3 *M. Crabbe-Mann¹, D. Tsaoulidis², M. Parhizkar¹, M. Edirisinghe^{*1}*

4 ¹*Department of Mechanical Engineering, University College London, London, WC1E 7JE, UK*

5 ²*Department of Chemical Engineering, University College London, London, WC1E 7JE, UK*

6 **Corresponding author email: m.edirisinghe@ucl.ac.uk*

7 **Abstract**

8 Cellulose derivatives (CD) are an attractive sustainable material used frequently in
9 biomaterials, however their solubility in safe, green solvents is not widely exploited. In this
10 work three cellulose derivatives; ethyl cellulose, cellulose acetate and carboxymethyl cellulose
11 were subjected to electrohydrodynamic processing (EHD). All were processed with safe,
12 environmentally friendly solvents; ethanol, acetone and water. Ethyl cellulose was electrospun
13 and an interesting transitional region was identified. The morphological changes from particles
14 with tails to thick fibres were charted from 17wt% to 25wt% solutions. The concentration and
15 solvent composition of cellulose acetate (CA) solutions were then changed; increasing the
16 concentration also increased fibre size. At 10wt% CA, with acetone only, fibres with heavy
17 beading were produced. In an attempt to incorporate water in the binary solvent system to
18 reduce the acetone content, 80:20 acetone/water solvent system was used. It was noted that for
19 the same concentration of CA (10wt%), the beading was reduced. Finally, carboxymethyl
20 cellulose (CMC) was electrospun with poly(ethylene oxide) (PEO), with the molecular weight
21 and polymer compositions changed and the morphology observed.

22 **Keywords:** *Cellulose derivatives, Green Solvents, electrohydrodynamic processing,*
23 *microstructures.*

24

25

26 **1. Introduction**

27 Electrohydrodynamic processing of cellulose derivatives (Son, Youk et al. 2003, Frenot,
28 Henriksson et al. 2007, Frey 2008) is becoming increasingly popular due to its sustainable
29 origins and its solubility in organic solvents. Cellulose derivatives (CD's) are commonly used
30 as biomaterials in drug encapsulation (Eltayeb, Bakhshi et al. 2013), wound patches (Son, Youk
31 et al. 2006) and even as a drug release controlling matrix in oral doses (Shokri and Adibki
32 2013). However, much of the processing involved uses solvents which are considered toxic
33 and harmful to the environment. Post processing such as freeze drying or vacuum drying are
34 options ensure any solvent residues are removed, although this will increase production time
35 and costs too. Whereas, this step can be avoided if safe solvents can be utilised instead. Although
36 CD's can be processed using safer solvents, it is overlooked due to the ease of processing with
37 solvents such as chloroform, N,N-dimethylacetamide, N,N-dimethylformamide and formic
38 acid (Tungprapa, Puangparn et al. 2007) used with cellulose acetate or 2,2,2-trifluoroethanol
39 (Jeun, Lim et al. 2007) and dichloromethane (Duarte, Gordillo et al. 2006) used with ethyl
40 cellulose. Electrospinning with organic solvents can be difficult i.e. the volatility of acetone
41 can cause blockages as the solution dries up and the high surface tension of water can also
42 cause difficulties.

43 The electrohydrodynamic processing of cellulose derivatives goes back to Formhals (Formhal
44 1934), where two of his original patents used cellulose acetate and propionyl cellulose to form
45 fibres. Electrohydrodynamic (EHD) processing is an easy and cost effective process (Reneker,
46 Yarin et al. 2000) that uses an electric field to distort a polymeric droplet by inducing repulsion
47 between the polymeric chains, thus overcoming the surface tension and allowing a jet to be
48 formed. Depending on the solution properties, primarily concentration, either electrospinning
49 or electrospraying will occur, thereby producing fibres or particles, respectively (Agarwal,
50 Wendorff et al. 2008). The EHD process is able to produce a range of structures; particles,

51 beaded fibres, smooth fibres and ribbons, making it attractive manufacturing procedure in
52 many industries (Agarwal, Wendorff et al. 2008). Solvent evaporation occurs as the jet travels
53 towards the collector (Shenoy, Bates et al. 2005), in the case solvent residues are present water
54 and ethanol would be preferable opposed to previous mentioned solvents.

55 In an effort to push CD's further as a biomaterial, the solvent problem must be tackled and
56 reported. Ethyl cellulose (EC) is non-ionic and hydrophobic but soluble in polar solvents such
57 as ethanol (Park, Kim et al. 2015). Previously implanted by Miyamoto et al. (Miyamoto,
58 Takahashi et al. 1989) showed EC was not absorbed by living tissue after implantation in dogs.
59 Electrospun CA is used widely in medical applications, such as cell culture and regenerative
60 medicine, and drug delivery (Cui, Zhou et al. 2016). CA has excellent water retention
61 properties, which is a desirable trait in wound dressing, where absorbing wound exudate is an
62 important function (Liu, Lin et al. 2012).

63 Carboxymethyl cellulose (CMC) is a water soluble derivative of cellulose, and a known
64 mucoadhesive (Brako, Raimi-Abraham et al. 2015).

65 There is a trend to embrace in “green” electrospinning which involves the use of solvents which
66 are typically non-toxic and biocompatible like ethanol or phosphate buffered saline (Castilla-
67 Casadiego, Maldonado et al. 2016). The choice of solvent must also be balanced against the
68 desired morphology, as different solvent systems have been used with varied results. As
69 Tunprapa et al. (Tunprapa, Puangparn et al. 2007) demonstrated with electrospun CA; in
70 acetone/dimethylacetamide 2:1, beaded fibres were produced whereas CA in
71 dichloromethane/methanol 4:1 formed smooth fibres. The use of volatile, organic solvents such
72 as acetone can give rise to porous or beaded fibre morphologies as it has a high evaporation
73 rate, conversely adding water can “smoothen out” fibres, as water has a higher viscosity than
74 acetone (Luo, Stride et al. 2012).

75 EC was processed using a binary solvent made from water and ethanol (EtOH) (Luo, Nangrejo
76 et al. 2010), despite its hydrophobic nature. Decreasing the EtOH content, reduces the potential
77 amount of EtOH residue in the final polymeric fibres/particles, which is a mild irritant (Loffler,
78 Kampf et al. 2007). It is ideal to keep the EtOH content to a minimum, however, this has to be
79 balanced against solubilizing the polymer. Increasing the proportion of water above 20% (v/v)
80 will form solid suspensions whilst further increase will show no solubility.

81 Previous investigations into the effect of solvent selection on the morphology of electrospun
82 CA fibres (Liu and Hsieh 2002, Tungprapa, Puangparn et al. 2007), however, were carried out
83 without a specific application in mind and therefore toxicology was not taken into
84 consideration.

85 Carboxymethyl cellulose has been predominantly used with water, with the exception of
86 Kessick and Tepper's (Kessick and Tepper 2003) work, where CMC was dissolved in a mixture
87 of methanol and water.

88 This work will demonstrate that ethyl cellulose, cellulose acetate, and carboxymethyl cellulose
89 can produce a wide range of microstructures with the one step EHD process, using
90 environmentally friendly solvent systems. This study focuses on optimising the processing
91 conditions of cellulose derivatives with the aim to produce non-woven fibrous wound healing
92 patches. The parameters studied were solution properties; concentration, solvent composition,
93 polymer molecular weight and polymer composition. Processing parameters were also altered,
94 specifically; applied voltage, flow rate, needle to collector distance and finally the effect of
95 attaching a guard plate to the EHD needle on the microstructures.

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100 **2. Experimental Details**

101 *2.1 Materials*

102 In the following table the polymers, additives, solvents and resulting solutions used in this work
 103 are described.

Material	Abbreviation	Molecular weight/g mol ⁻¹	Degree of substitution	Concentration/wt%	Solvent
Ethyl cellulose	EC	22,800	48% ethoxyl	17-25	Ethanol/ water at 80:20 (v/v)
Cellulose acetate	CA	30,000 M _n	39.8% acetyl	10, 12.5, 15 and 17.5	Acetone
				10	Acetone/ Water at 80:20 - 100:0 (v/v)
Sodium Carboxymethyl cellulose	CMC 25	250,000	0.9 carboxymethyl groups per anhydroglucose group	4	Water
Sodium Carboxymethyl cellulose	CMC 70	700,000	0.9 carboxymethyl groups per anhydroglucose group	1	Water
Poly(ethylene oxide)	PEO	200,000 M _v		15	Water

104 **Table 1:** Materials used in this work. Molecular weight is M_w unless indicated. Where M_n is molecular
 105 number and M_v is molecular volume.

106

107 *2.2 Solution Preparation*

108 Ethyl cellulose 5-30wt% and 17-25wt% were dissolved in ethanol and distilled water (80:20
 109 vol. ratio), respectively. Cellulose acetate 10, 12.5, 15, and 17.5wt% were dissolved in acetone
 110 only. Cellulose acetate 10wt% were dissolved in 100:0, 95:5, 90:10, 85:15, 80:20 acetone:
 111 water (vol. ratio). Carboxymethyl cellulose/PEO solutions were made at 25:75, 14:86 and
 112 10:90 wt. ratio with CMC M_w equal to 250,000 and 14:86 wt. ratio with CMC M_w equal to

113 700,000. The polymer solutions were mixed at ambient temperature and humidity (21 °C and
114 40-50 %, respectively) for 24-72 hours, depending on the concentration, , until a homogenous
115 solution formed

116

117 *2.3 Solution Characterisation*

118 Viscosity, surface tension, electrical conductivity, and density were characterised for each of
119 the solutions used. Viscosity measurements were conducted using a U-tube viscometer (size G
120 and H, VWR, UK). Surface tension was measured with a tensiometer (Kruss K100, Kruss
121 GmbH, Hamburg, Germany) using the Wilhelmy's method. The electrical conductivity was
122 measured using a conductivity meter (Jenway 3450, Bibby Scientific Limited, Staffordshire,
123 UK). The density was measured using a standard 5 ml density bottle. All measurements were
124 taken at ambient temperature and humidity (21 °C and 40-50%, respectively). Values are given
125 in Tables 4-6. Each characterisation was tested 10 times and standard deviation was calculated.
126 The standard deviation for surface tension was 0.1 mN m⁻¹, 2.1 mPa s for viscosity and 1.6 μS
127 m⁻¹ for electrical conductivity measurements. All equipment used were calibrated with ethanol
128 prior to use.

Solution /wt%	Density /kg m ⁻³	Viscosity /mPa s	Surface Tension /mN m ⁻¹	Electrical Conductivity /μS m ⁻¹
5	3980	30.5	18.7	55.4
10	4290	151.0	23.8	61.4
15	4450	539.0	24.0	64.4
20	4520	800.5	26.7	62.5
25	4640	1652.5	27.4	57.8
30	4700	3008.2	35.2	51.4

129 **Table 2:** Characteristics of ethyl cellulose 5-30wt% solutions used.

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Solution /wt%	Density /kg m ⁻³	Viscosity /mPa s	Surface Tension /mN m ⁻¹	Electrical Conductivity /μS m ⁻¹
17	4450	613.0	24.7	64.4
18	4460	691.3	24.8	64.0
19	4505	750.5	25.2	63.1
20	4520	800.5	26.6	62.5
21	4550	936.7	26.6	62.0
22	4620	1110.6	26.8	61.4
23	4640	1179.6	26.9	61.0
24	4640	1277.9	26.9	59.6
25	4640	1652.5	27.7	57.8

134 **Table 3:** Characteristics of ethyl cellulose 17-25wt% solutions used.

Solution /wt%	Solvent composition	Density /kg m ⁻³	Viscosity /mPa s	Surface Tension /mN m ⁻¹	Electrical conductivity /μS m ⁻¹
10	100% Acetone	823	25.8	23.8	3.8
12.5		832	33.9	21.8	3.8
15		839	65.2	21.3	4.0
17.5		848	154	22.1	3.9
10	80% Acetone	896	65.8	28.6	8.6
10	85% Acetone	874	42.7	26.6	8.4
10	90% Acetone	856	36.0	25.2	8.7
10	95% Acetone	838	27.4	25.0	6.7

135 **Table 4:** Characteristics of cellulose acetate solutions used.

M_w /g mol ⁻¹	Solution /wt%	Density /kg m ⁻³	Viscosity /mPa s	Surface Tension /mN m ⁻¹	Electrical conductivity /μS m ⁻¹
250,000	25:75	1088	855.1	58.1	827.2
	14:86	1066	743.9	51.4	498.5
	10:90	1056	603.9	49.2	390.4
700,000	14:86	1034	535.9	51.1	371.2

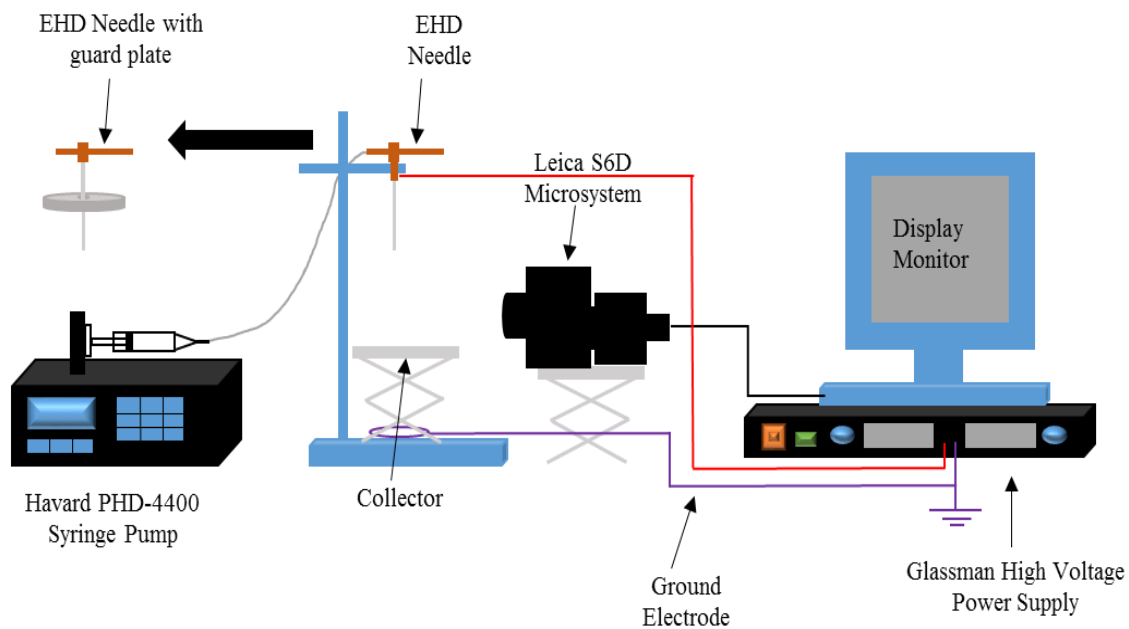
144 **Table 5:** Characteristics of carboxymethyl cellulose solutions used.

145

146 *2.4 Experimental setup for particle/fibre production*

147 Figure 1 illustrates the EHD experimental setup used. The solution was loaded into 10 mL
148 syringes (Becton and Dickinson Company, Oxford, UK) attached with 0.76 mm inner diameter
149 capillary tubing (Sterilin, UK) to the stainless steel needle (15 G, ID: 2.06 mm, OD: 2.67 mm,
150 Stainless Tube & Needle Co Ltd, Staffordshire, UK). The flow rate was controlled by a syringe

151 pump (PHD 4400, Harvard Apparatus, Edenbridge, UK). The needle was attached to a high
 152 precision voltage generator (FC 120 W, Glassman Europe Limited, Bramley, UK) with
 153 capability of 0 – 30 kV output. The ground electrode was attached to the metal collector. The
 154 solutions were subjected to a range of voltages (0-20 kV), the flow rates used were 50 and 100
 155 $\mu\text{l min}^{-1}$, and distance from collector to tip was 100 and 150 mm. Samples were collected on
 156 glass microscope slides. All experiments were carried out at ambient conditions (21 °C and 40-
 157 50% humidity). A metallic plate, known as a guard plate, was attached to the steel needle and
 158 experiments conducted to evaluate its effect on microstructure morphology.



159 **Figure 1:** Schematic of the EHD set up.

160 *2.5 Sample Characterisation*

161 To observe the product shape, size, and morphology, samples were collected on glass
 162 microscope slides and images were obtained using an optical microscope (Zeiss Axiotech)
 163 fitted with a Q-imaging Micropublisher 3-3RTV camera. Scanning electron microscopy
 164 (Hitachi S-3400n), was performed on samples which were vacuum coated with gold for 90
 165 s. All images were analysed using ImageJ (public domain open source image processing
 166 software available online). The error bars shown in Figures 4-7, 9 and 11 indicate the standard
 167 deviation of the measurements, where n=100.

168 **3. Results and Discussion**

169 *3.1 Ethyl Cellulose*

170 *3.1.1 Effect of concentration on microstructures*

171 Initially, solutions of 5, 10, 15, 20, 25 and 30wt% were made and processed via EHD. Solutions
172 of 5, 10 and 15wt% produced particles with the average diameter of 2.3, 3.0 and 3.2 μm ,
173 respectively. At these concentrations electrospinning occurred due to the lack of chain
174 entanglements; physical interlocking of the polymer chains in solution (Husain, Lau et al.
175 2016). Solutions with low viscosities were more prone to the effect of the Rayleigh-Plateau
176 instability brought on by surface tension (i.e. waves of instability along the jet cause it to break
177 up into droplets resulting in particles) (Luo and Edirisinghe 2014).

178 As the droplet traversed towards the collector, the solvent evaporated, causing an increase of
179 the charge density of the droplet until it reached a maximum value, known as the Rayleigh
180 limit. At this point Coulomb fission occurred; this is a phenomenon where a droplet at its
181 Rayleigh limit will eject some of its content in the form of “secondary” or “daughter” droplets,
182 thereby reducing the charge of the “parent” droplet and its size (Almeria, Deng et al. 2010),
183 this can bring about polydispersity in the sizes of the particle produced. Coulomb fission
184 became increasingly apparent from figure 2A to 2C. **Lower viscosity solutions are more
185 susceptible to the effect of surface tension which promotes electrospinning rather than
186 electrospinning, producing particles (Deitzel, Kleinmeyer et al. 2001).**

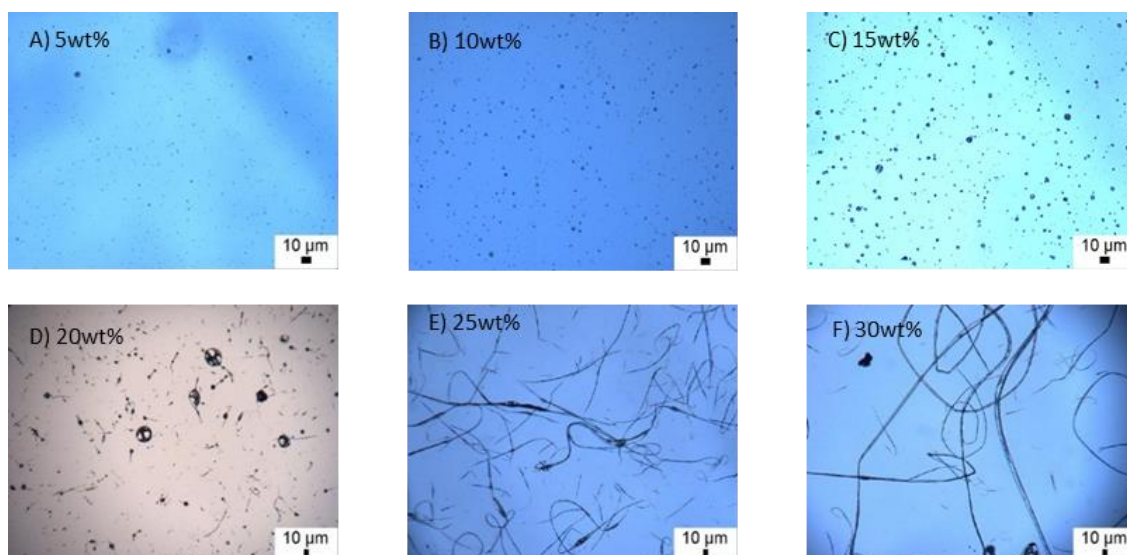
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192 **Figure 2:** Optical micrographs of EC microstructures produced by EHD processing (applied voltage,
 193 flow rate and collection distance were 15 kV, 100 $\mu\text{L min}^{-1}$ and 100 mm, respectively)

194

195 The concentration of chain entanglements is controlled by polymer molecular chain length and
 196 solution polymer concentration. Increasing these simultaneously or individually will lead to an
 197 increase in chain entanglements pushing electrospinning to electrospinning (Shenoy, Bates et
 198 al. 2005, Almeria, Deng et al. 2010). When the entanglements between the polymer chains in
 199 the solution reach a critical level the jet is no longer able to break up; this brings about fibre
 200 formation (Li and Wang 2013). The increase in viscosities listed in Table 4, from 613 to 1652.5
 201 mPas, verify this increase of polymer chains present, and the transition is shown in Figures 2C
 202 to 2E.

203 At 20wt%, particles with tails began to emerge. The increase in concentration enabled
 204 electrospinning creating the tails, however, the Rayleigh-Plateau instability had not been
 205 completely overcome.

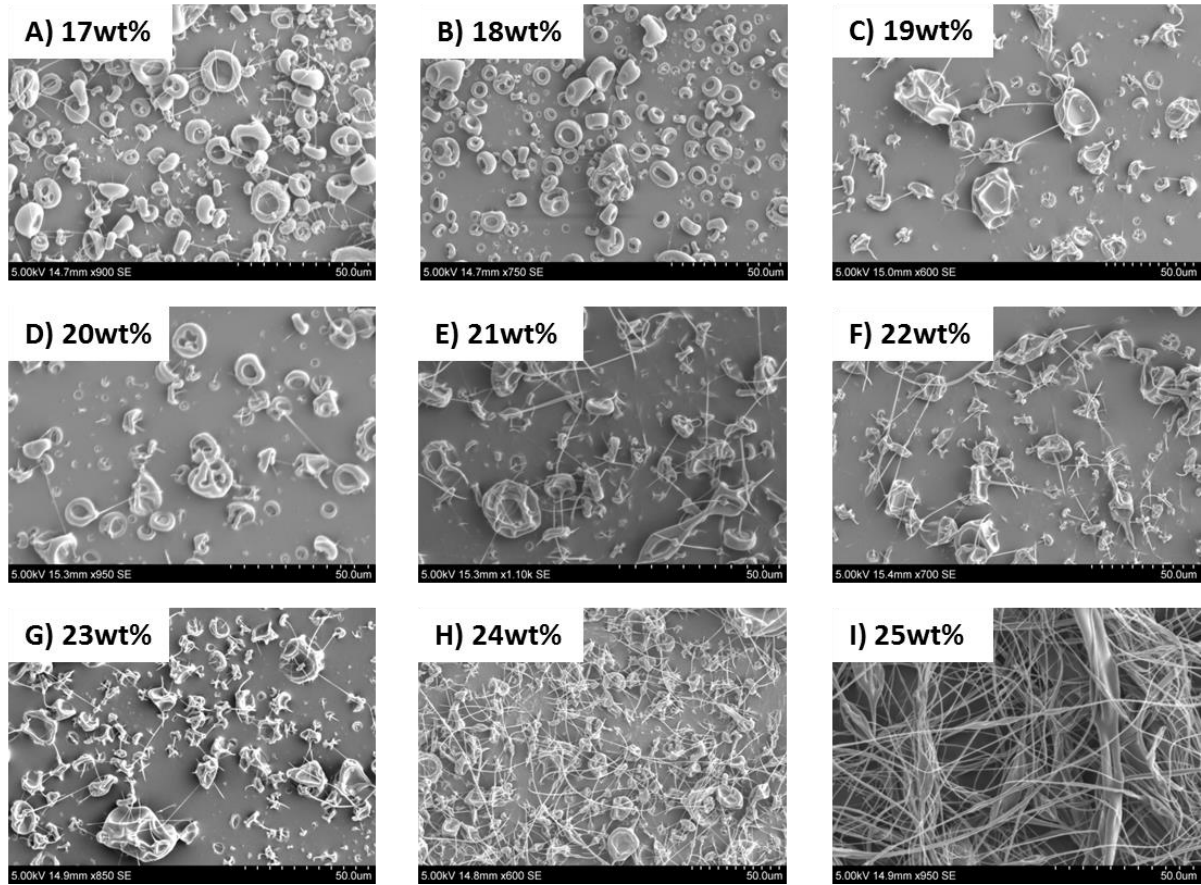
206 At 25wt% of EC, fibres were produced as a result of electrospinning. The fibres produced had
 207 an average diameter of 3.8 μm . The lack of spherical beads present on the fibre indicates the
 208 surface tension had been overcome despite the high value, 27.69 mN m^{-1} . For highly viscous
 209 liquids (1652.5 mPas) the jet does not break up, instead, it travels as a whipping jet towards the

210 grounded target (Taylor 1964). Surface tension plays a less significant role at higher viscosities,
211 also enabling fibre formation (Deitzel, Kleinmeyer et al. 2001). The 30wt% solution produced
212 thick, ribbon-like fibres with an average width of 4 μm . Electrospinning with this solution was
213 difficult due to the high polymer content. High polymer content meant rapid solvent
214 evaporation, which caused blockages in the needle.

215 From these experiments, it was clear that there was an interesting region of transition between
216 15 to 25wt%, which required further investigation. To chart the transition, smaller increments
217 of concentration were tested, solutions of 17, 18, 19, 20, 21, 22, 23 and 24wt% were also
218 subjected to EHD and the gradual transition from particles to fibres was observed. Figure 3
219 displays the different morphologies produced as a result of changes in concentration (17-
220 25wt%). At 17wt%, the chain entanglements were not sufficient enough to prevent the jet
221 break-up and particles were still present. However, the viscosity of 17wt% was 74 mPa s higher
222 than 15wt%, resulting in these particles having short tails.

223 Conversely, at 25wt%, the Rayleigh-Plateau instability had the least effect, which was evident
224 by the lack of particles. When the electric field is applied, the electric force causes repulsion
225 between polymer chains and forces the droplet to expand, which opposes the surface tension
226 of the droplet trying to maintain the spherical shape and reduce the systems energy. As the
227 charge builds, the repulsion overcomes the surface tension and with sufficient polymer
228 entanglements, the well-known Taylor cone is formed and a jet is emitted (Garg and Bowlin
229 2011). However, the formation of beaded fibres shows the Rayleigh-Plateau instability is still
230 present and had not been entirely overcome (Luo and Edirisinghe 2014).

231



232 **Figure 3:** Scanning electron micrographs of EC microstructures produced by EHD processing (applied
 233 voltage, flow rate and collection distance were 19 kV, 100 $\mu\text{L min}^{-1}$ and 150 mm, respectively).

234

235 As the concentration increased, the resistance to Rayleigh-Plateau instabilities increased and
 236 the jet was less susceptible to break up (made longer fibres) and disturbances (caused less
 237 beading), as shown in Figure 3. Processing solutions above 25wt% was difficult, and
 238 continuous electrospinning was not possible due to repeated blockages. The 25wt% solution
 239 was deemed as the most desirable concentration of EC for uninterrupted fibre formation.

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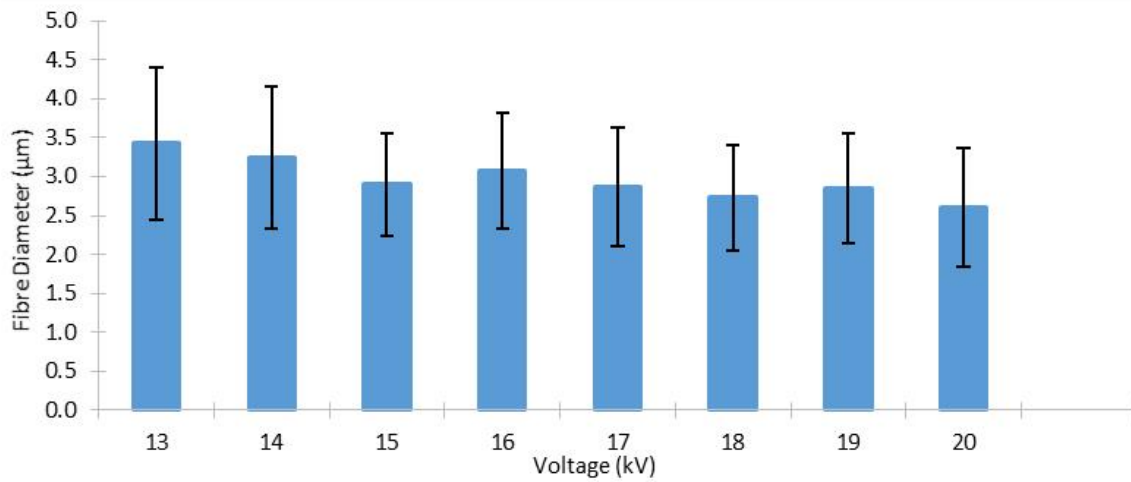
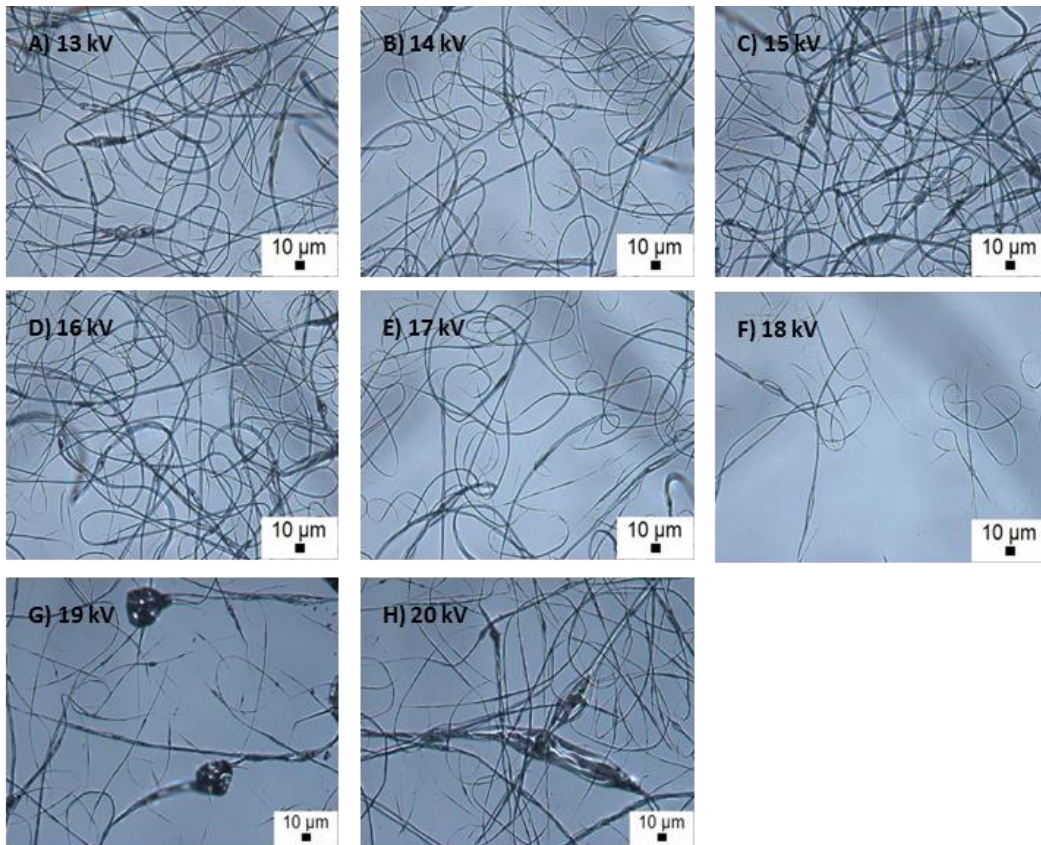
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245 3.1.2 *Effect of applied voltage on microstructure*

246 The effect of voltage on fibre diameter is disputed in the literature, with no consensus whether
247 there is a positive or negative correlation between the fibre diameter and voltage. Yuan et al.
248 (Yuan, Zhang et al. 2004) showed a reduction in fibre diameter with an increase in voltage in
249 their polysulfone/dimethylacetamide/acetone system. When the voltage is applied, it causes an
250 increase in the net charge of the jet, improving the whipping instability and stretching resulting
251 in production of thinner fibres (Hohman, Shin et al. 2001). On the contrary Zhang et al. (Zhang,
252 Yuan et al. 2005), while working with a polyethylene oxide/water system showed an increase
253 in fibre diameter with increasing voltage. The increase in voltage caused higher jet speed,
254 reducing the flight time of the jet and the time allowed for the solvent to evaporate leading to
255 thicker fibres (Hayati, Bailey et al. 1986) . In the case of EC, as the voltage was increased,
256 fibres with smaller diameters were obtained (Figure 4).

257 For this concentration, 25wt%, it appeared that the intermediate voltages, i.e. 16-18 kV, were
258 the most stable, affected minimally by instabilities as shown by the lack of beading in fibres
259 (Figures 4D-F). This high concentration had an increased number of polymer chains per unit
260 volume of the solution, which means the effect of repulsion was greater. At 19 kV (Figure 4G),
261 for the given flow rate ($50 \mu\text{L min}^{-1}$), a stable cone jet was not formed. Rayleigh-Plateau
262 instabilities became a dominant factor and this was evident by presence of circular beads.

263 Changing the voltage, independent of the flow rate, increased the possibility of forming beaded
264 fibres; for each flow rate there was a “critical voltage” where a stable Taylor cone formed,
265 producing smooth fibres (Garg and Bowlin 2011). At 20 kV, the fusion of beads occurs, which
266 brings down the fibre diameter. Higher electrical field strength, increases the repulsive forces
267 acting on the polymer chain, thereby increasing the stretching that leads to a reduction in fibre
268 diameter (Zhang, Yuan et al. 2005).



269 **Figure 4:** Optical micrographs of EC microstructures produced by EHD processing (concentration,
 270 flow rate and collection distance were 25wt%, 50 $\mu\text{L min}^{-1}$ and 100 mm, respectively), and variation in
 271 fibre diameter with voltage.

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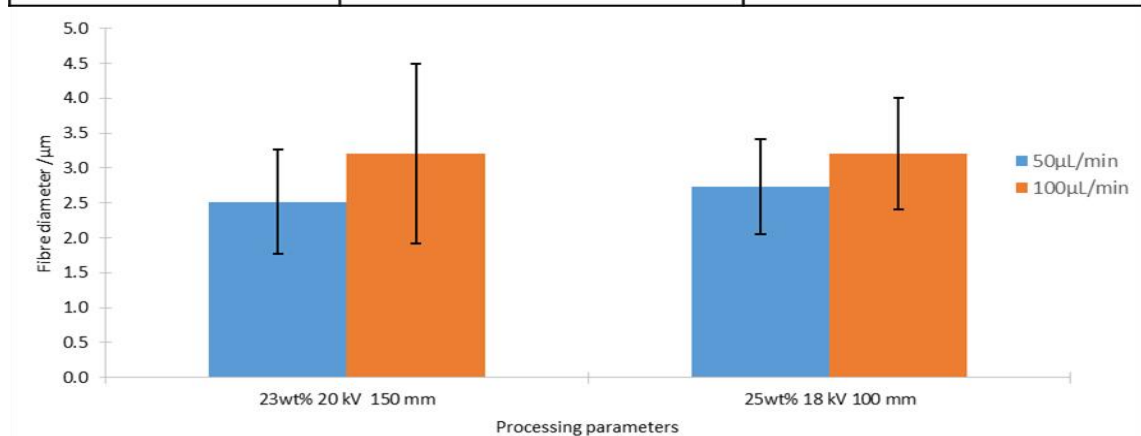
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275 3.1.3 Effect of flow rate on microstructure

276 Changing the flow rate had a marked effect on morphology, as shown in Figure 5. Increased
 277 flow rate increased the fibre diameter and droplet/bead diameter. When a larger volume of
 278 solution streams from the needle tip per unit time i.e. $100 \mu\text{L min}^{-1}$, the reduced solvent
 279 evaporation formed larger fibres and beads compared to microstructures produced at $50 \mu\text{L min}^{-1}$.
 280 min^{-1} . The increased flow rate allows for fewer stretching forces (Li and Wang 2013), as under
 281 the same voltage, the same amount of energy competes to repel a greater number of polymer
 282 chains flowing through the needle tip. This same amount of energy cannot reproduce the same
 283 repelling forces for a greater flow rate (i.e. greater volume), hence larger fibres were produced.

Concentration & Applied Voltage	Flow rate: $50 \mu\text{L min}^{-1}$	Flow rate: $100 \mu\text{L min}^{-1}$
23wt%, 19kV		
25wt%, 17kV		



284 **Figure 5:** Scanning electron micrograph of EC microstructures produced by EHD processing with
285 graph showing fibre diameter variation with flow rate (collection distance was 100 mm). Samples were
286 collected over 30 s.

287

288 The concentrations shown in Figure 5; 23 and 25wt% and were processed with identical
289 parameters. At a lower flow rate the difference in fibre diameter between 23 and 25wt% is
290 palpable, however, at $100 \mu\text{L min}^{-1}$ the diameters converge, which indicated the flow rate was
291 limiting the extent the fibre diameter can be increased.

292

293 3.1.4 Effect of collection distance on microstructure

294 The dominant effect brought about by changing the distance between the tip and the collector,
295 is the time allowed for solvent evaporation. Increasing this distance, increased the flight time
296 and in turn, the time allowed for solvent evaporation to occur which decreased the fibre/bead
297 diameter. As the jet traversed towards the collector, both internal charges and the external
298 electric field induced a whipping motion which works to stretch the polymer chains, reducing
299 the fibre diameter (Deitzel, Kleinmeyer et al. 2001). It is also at this point where solvent
300 evaporation occurs, reducing the fibre diameter. Table 7 demonstrates the change in fibre
301 diameter, fibres collected at 150mm have a smaller diameter compared to 100mm. **The solution**
302 **with 24wt% EC was able to form thinner fibres, albeit with slight beading, as it has a higher**
303 **electrical conductivity compared to 25wt% (Table 5) as increased conductivity leads to thinner**
304 **fibres.**

Concentration	Tip to collector distance:100mm	Tip to collector distance:150mm
24wt%	2.52 ± 0.64	1.37 ± 0.34
25wt%	3.5 ± 0.98	2.5 ± 0.52

305

306 **Table 6:** Fibre diameter as a function of tip to collector distance, for 24 and 25wt% ethyl cellulose
307 solutions

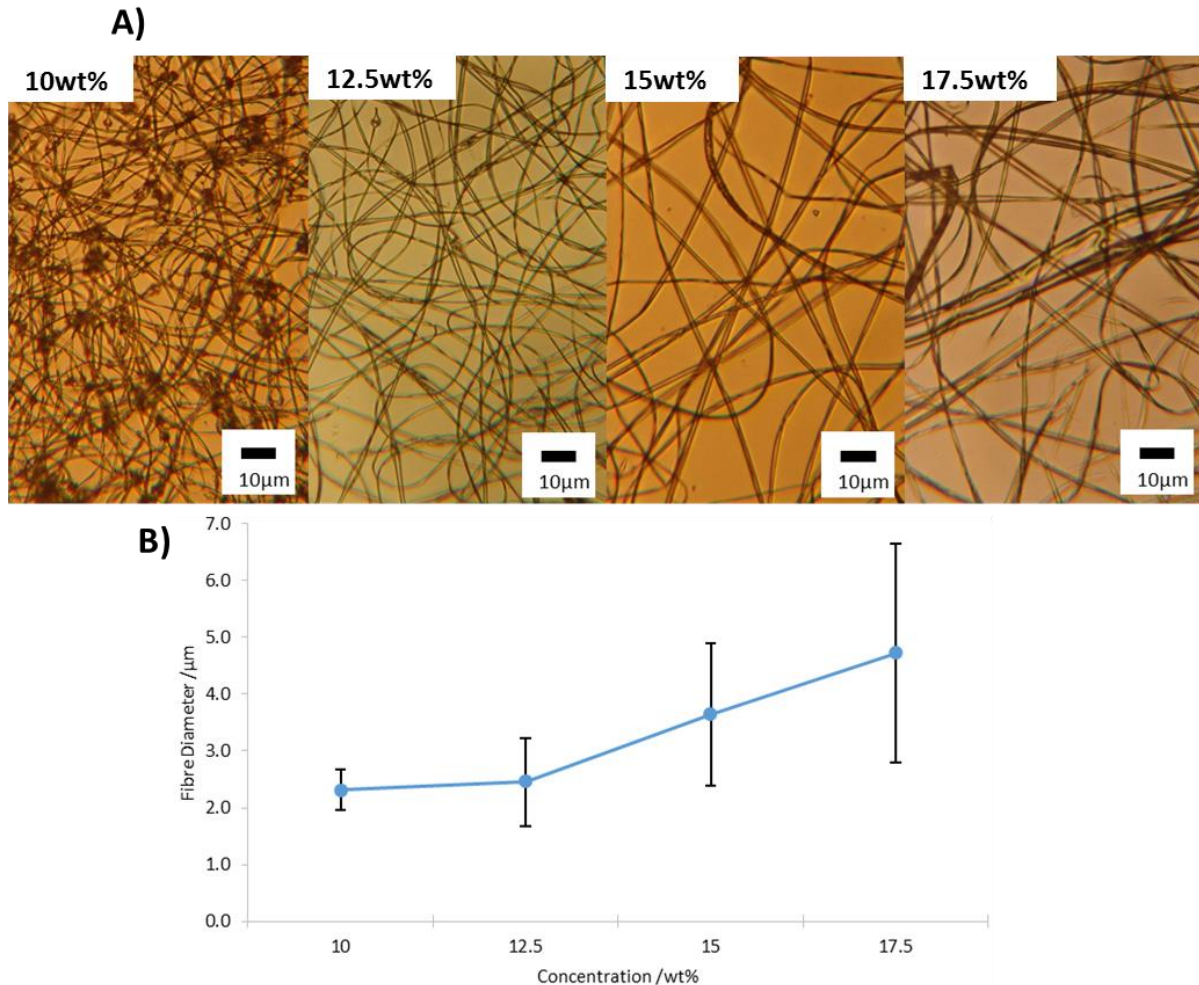
308 3.2 Cellulose Acetate

309 3.2.1 Effect of concentration on microstructure

310 Solutions of 10-17.5wt% of cellulose acetate were electrospun. The effect of concentration is
311 similar to that discussed for EC. Figure 6B shows a positive correlation between the polymer
312 concentration and fibre diameter. As with EC, the increase in CA concentration increased the
313 entanglement between the molecular chains.

314 Figure 6A displays the change in morphology as the concentration increases. At 10wt%, the
315 fibres are heavily beaded and have the smallest fibre diameter at 2.32 μ m. Although the
316 concentration is high enough to bring about electrospinning, demonstrated by the presence of
317 fibres, the viscosity was not high enough to resist the instabilities, along with the highly volatile
318 nature of acetone, beads were formed (Li and Wang 2013). Increasing the concentration to
319 12.5wt%, produced fibres with much less beading.

320 At concentration 15wt%, the fibre diameter increased to 3.62 μ m. Increasing the concentration
321 makes the solution less prone to the drawing process which stretches the jet as it whips towards
322 the collector, resulting in larger diameters. Concentration 17.5wt% produced the fibres with a
323 diameter of 5.5 μ m, showing this concentration was the most resistant to the stretching due to
324 the high level of chain entanglements preventing this.



325 **Figure 6:** A) Optical micrographs of CA microstructures produced by EHD processing with the
 326 following solution concentrations L-R 10, 12.5, 15 and 17.5wt% in acetone only

327 B) Variation in fibre diameter with polymer concentration (applied voltage, flow rate and collector
 328 distance were 12 kV, 6 mL h⁻¹ and 100 mm, respectively).

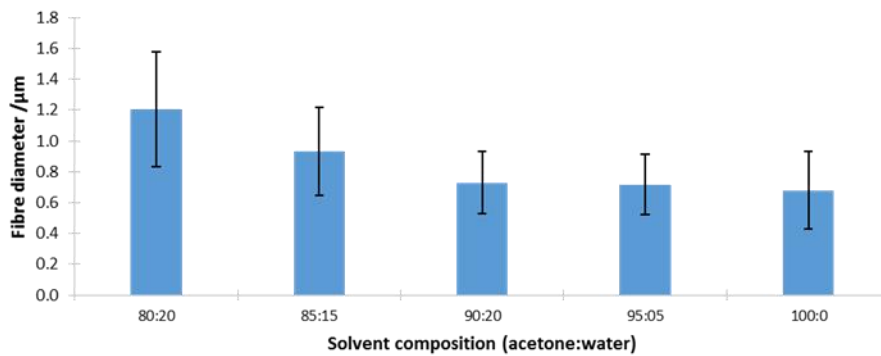
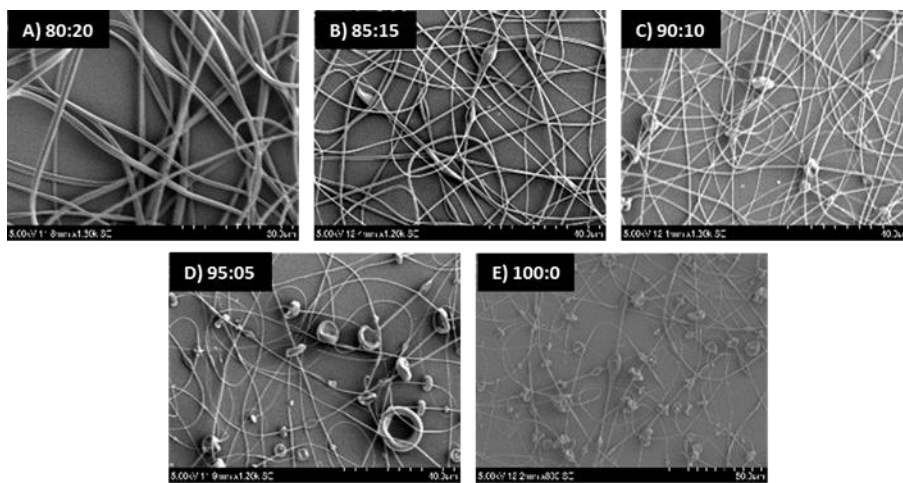
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330 3.2.2 Effect of solvent on microstructure

331 In an attempt to reduce the beading in the 10wt% sample (Figure 6A), water was added in
 332 increments of 5% (vol.) and the morphological changes were observed. Water is a non-solvent
 333 for CA, but can be added to acetone on order to reduce the evaporation rate and change the
 334 fibre diameter (Frey 2008). **Adding water to the solution had a noticeable effect on the fibre**
 335 **morphology as shown in Figure 7. It simultaneously reduced the beading and increased the**
 336 **fibre diameter. Concave beads were still found on the fibres (Figures 7C-E) with higher acetone**

337 **content.** These concave structures arise as a consequence of the volatility of acetone; acetone
338 has an evaporation rate of 5.6 compared to water which is 0.3 (Smallwood 1996). Thus, this
339 hinders polymer diffusion which led to the formation of hollow beads with concave structures
340 (Lee, Kim et al. 2003) rather than solid, spherical beads. Reducing water content reduced the
341 viscosity of the liquid, therefore instabilities were able to influence the jet and give rise to
342 beading (Luo, Stride et al. 2012).

343



344 **Figure 7:** Scanning electron micrographs of CA microstructures produced by EHD processing and
345 variation in fibre diameter with solvent composition (concentration, applied voltage, flow rate and
346 collector distance were 10wt%, 13 kV, 4 mL h⁻¹ and 100 mm, respectively).

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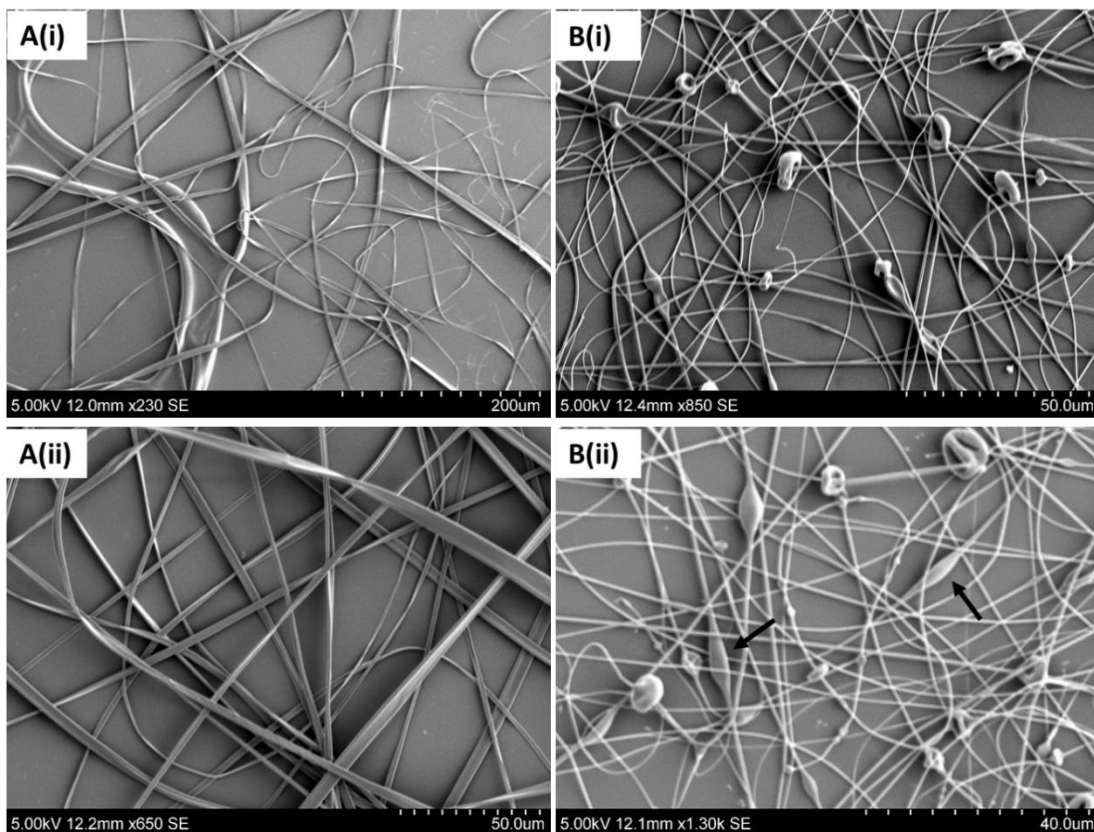
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351 3.2.3 *Effect of guard plate on microstructure*

352 The guard plate can be added to an EHD set up to strengthen the electric field and to control
353 the deposition area of the fibres. In this investigation, the effect on the fibre diameter was
354 examined. The solutions which produced the largest diameter, 17.5wt%, and solution which
355 gave the most beaded sample, 10wt%, both with 80:20 acetone/water solvent system, were
356 tested using the guard plate. The guard plate reduced fibre dispersity of samples collected from
357 17.5wt%; from 0.54 (Figure 8A (i)) to 0.49 (Figure 8A (ii)). Fibres collected from 10wt%
358 (Figures 8B (i-ii)) showed a reduction in beading on the fibres upon adding the guard plate.
359



360 **Figure 8:** Scanning electron micrographs of CA microstructures produced by EHD processing

361 (concentration, voltage, flow rate, collection distance and solvent system were (A) 17.5wt%, 13 kV, 4
362 ml h⁻¹ and 100 mm, in acetone only (i) no guard plate and (ii) with guard plate, (B) 10wt%, 13 kV, 4 ml
363 h⁻¹ and 100 mm, in 80:20, (i) no guard plate and (ii) with guard plate, respectively).

364

365 The guard plate strengthens the electric field, which affected the whipping instability; a larger
366 force was exerted on the jet increasing the speed, and in turn increasing the stretching resulting
367 in reducing the fibre diameter (Yang, Jia et al. 2008) and suppressing the formation of rounded
368 beads. Figures 8B (i) to (ii) shows the suppression of some beads to elongated/spindle like
369 beads along the fibre, as indicated by arrows.

370

371 *3.3 Carboxymethyl Cellulose*

372 Poly(ethylene oxide) was added to the carboxymethyl cellulose (CMC) solution to act as a
373 spinning agent, as on its own, CMC cannot be electrospun (Brako, Raimi-Abraham et al. 2015).
374 This blend was made up of 4wt% carboxymethyl cellulose in water and 15wt% poly(ethylene
375 oxide) in water. These two solutions were mixed at the following ratios 90:10, 86:14 and 75:25
376 as used by Brako et al. (Brako, Raimi-Abraham et al. 2015) with two different molecular
377 weights of carboxymethyl cellulose; 250,000 and 700,000 g mol⁻¹.

378

379 *3.3.1 Effect of molecular weight on microstructure*

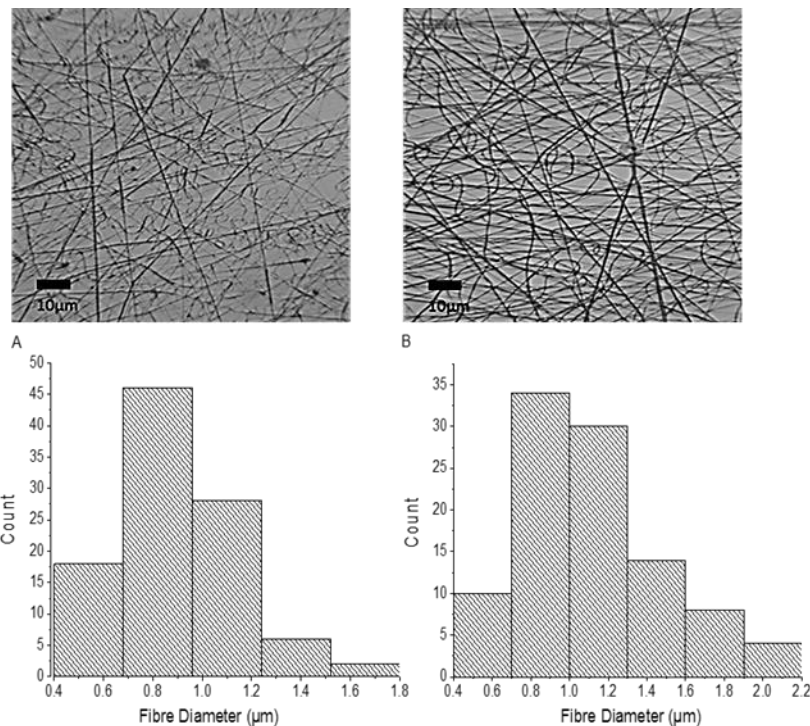
380 **Fibres produced from CMC70/PEO blend had a larger diameter compared to CMC25/PEO.**
381 **The longer polymer chain found in CMC70 participated in more physical entanglements to**
382 **such a degree that the drawing forces were resisted, leading to a larger average fibre size of**
383 **1.12 µm compared to 0.89 µm for CMC25/PEO fibres.**

384 **Changing the molecular weight caused a change in morphology as shown in Figure 9. The**
385 **fibres produced from 250,000 g mol⁻¹ had more bends than the products of 700,000 g mol⁻¹. As**
386 **mentioned previously, lower molecular weight is more susceptible to the instabilities brought**
387 **on by the electrical field, resulting in a twisted appearance. The bending or “buckling” are**
388 **formed by molecular repulsion in the jet (Han, Reneker et al. 2007).**

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Molecular weight /g mol ⁻¹	Fibre diameter / μm
250,000	0.89 ± 0.35
700,000	1.12 ± 0.23

Table 7: Fibre diameter as a function of molecular weight; 86:14 CMC/PEO w/w.

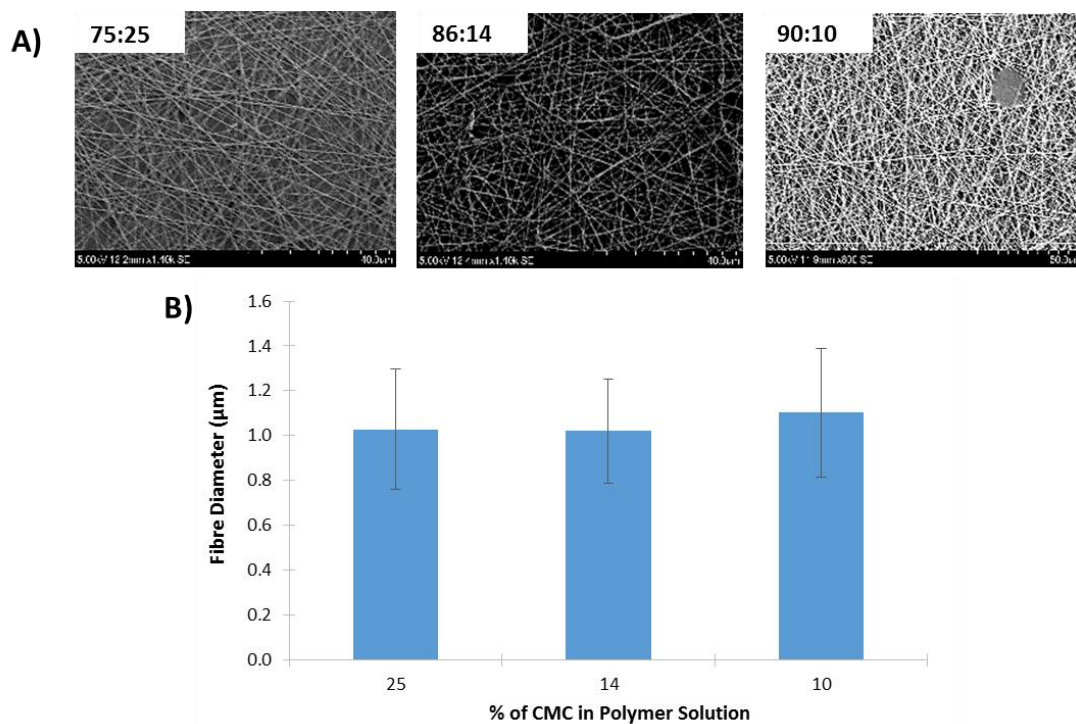


396 **Figure 9:** Optical micrographs of CMC/PEO fibres L-R 250,000 g mol⁻¹ and 700,000 g mol⁻¹ (voltage,
397 flow rate and collection distance were 15 kV, 5 $\mu\text{L min}^{-1}$ and 100 mm, respectively).

398

399 3.3.2 Effect of CMC/PEO content on microstructure

400 An increase in CMC content in the blend drove down the fibre diameter as shown by Figure
401 10. CMC has a greater chain length compared to PEO, 250,000 and 200,000 g mol⁻¹,
402 respectively. Enlarging the CMC25 content rather than PEO meant more polymer chain
403 entanglements were occurring, but not to the extent of CMC70 as previously mentioned. This
404 level of chain entanglement did not hinder the drawing process, instead making the fibres more
405 prone to the stretching phase of the electrospinning process and resulting in smaller fibre
406 diameter (Shenoy, Bates et al. 2005).



407 **Figure 10:** A) Scanning electron micrographs of CMC 25/PEO fibres at the following blends
 408 PEO:CMC a) 90:10, b) 86:14 and c) 75:25. B) Graph showing effect of CMC proportion in solution
 409 on fibre diameter. (Samples were collected at 15 kV, with 5 $\mu\text{L min}^{-1}$ flow rate with 100 mm needle tip
 410 to collector distance.)

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426 4. Conclusions

427 Cellulose derivatives, are commonly processed with unfavourable solvents. If cellulose
428 derivatives are to play a bigger role in medical materials, this has to be addressed. In this work,
429 a range of microstructures were produced with three cellulose derivatives, all solubilised in
430 non-toxic solvents, whilst using electrohydrodynamic processing. After initial experiments
431 with EC and CA further tests were carried out to delve deeper in the electrospinnability of these
432 polymers in safe solvents. EC had a transitional period of interest, 17-25wt%, this was further
433 investigated to identify how the structures transitioned from particle to fibre. Beyond 25wt%
434 was proven difficult to electrospin, however, this concentration gave continuous fibres, while
435 using the non-toxic binary solvent system of ethanol and water. CA was electrospun with
436 acetone, however, samples collected from 10wt% was heavily beaded. The solvent system was
437 adjusted and 20% (vol.) water was added to acetone in order to reduce the evaporation rate,
438 producing smooth fibres. This finding showed instead of increasing polymer concentration to
439 reduce beading, manipulating the solvent system alone brought about the same effect. Adding
440 the guard plate also played a role in reducing beading effect and fibre size. CMC with M_w
441 700,000 led to larger fibres compared to M_w 250,000. In the CMC/PEO blend, increasing the
442 content of polymer with higher M_w from 1.03 to 1.10 μm . This gives two routes/options to
443 adjust the fibre diameter or even the morphology of the fibre (either by varying the CMC
444 concentration, or by changing the molecular weight). Despite the challenge with
445 electrohydrodynamic atomization using organic solvents, this work has shown the potential to
446 produce a range of structures across three CD's with environmentally friendly solvents which
447 could potentially replace the use of cellulose in biomedical materials.

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