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NADES-derived beta cyclodextrin-based polymers as sustainable precursors to produce sub-micrometric cross-linked mats and fibrous carbons

This is a pre print version of the following article:

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1873631> since 2022-12-16T10:23:43Z

Published version:

DOI:10.1016/j.polymdegradstab.2022.110040

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(Article begins on next page)

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2 **micrometric cross-linked mats and fibrous carbons**

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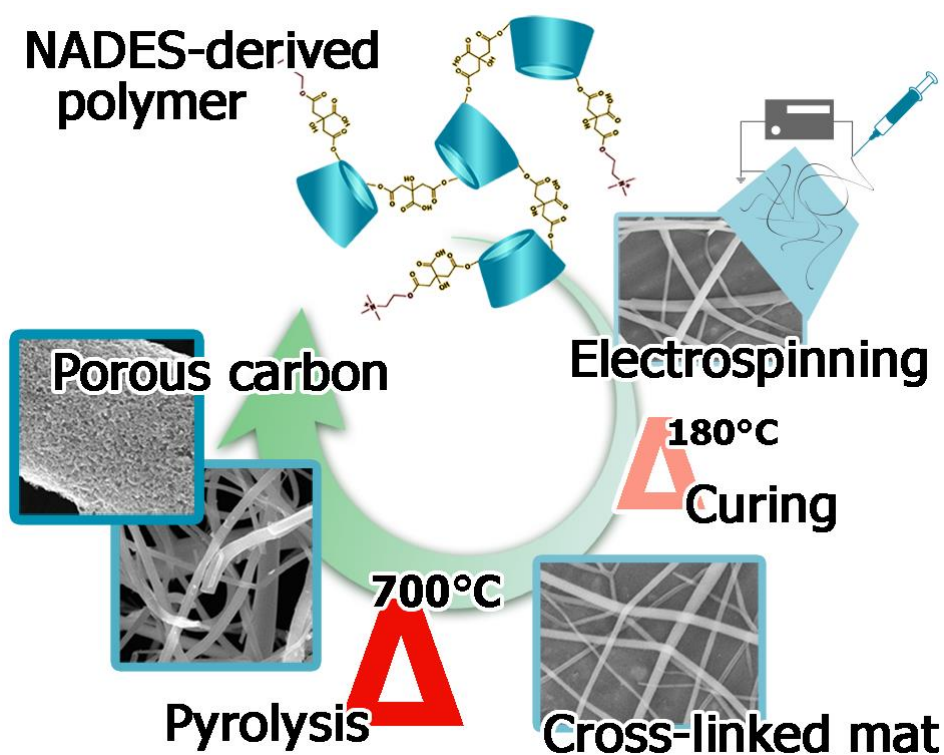
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11 **Graphical abstract**

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24

25 **Abstract**

26

27 Owing to their tuneable synthesis, good chemical stability, and biocompatibility, beta cyclodextrin (β CD)-
28 based polymers have attracted scientific and industrial attention. Besides, to render their fabrication more
29 sustainable and suitable for large-scale productions, the substitution of toxic compounds and organic solvents
30 with eco-friendly alternatives represents an active field of research. In this context, natural low-cost
31 compounds such as sugars, carboxylic acids, and amino acids, have been extensively reported as suitable
32 precursors to produce the so-called natural deep eutectic solvents (NADES). Furthermore, citric acid/choline
33 chloride NADES systems have been exploited as suitable solvent/reactive media for the synthesis of functional
34 water-soluble β CD-based polymers. In this work, the production of sub-micrometric fibres, from the
35 electrospinning of NADES-derived β CD-based polymer solutions, was investigated, using water as a unique
36 solvent. Also, the possibility to cross-link the obtained fibres via facile thermal treatment, without altering the
37 fibrous morphology was demonstrated. Accordingly, cured, insoluble fibrous mats with mean diameters of
38 $0.61\pm 0.15\ \mu\text{m}$ were obtained. Furthermore, the spun mats were screened as suitable bio-derived precursors to
39 produce porous carbon fibres. Average diameters lower than 500 nm were obtained as a result, while the use
40 of polyethylene oxide as a pore initiation agent, allowed to observe carbon fibres with porosities ranging from
41 13 to 24 nm. Eventually, the adsorption performances of both the cross-linked mat and the carbon fibres were
42 tested for the treatment of emerging pollutants in contaminated water.

43

44 **Keywords:**

45 Cyclodextrins, natural deep eutectic solvents, bio-derived polymers, electrospinning, carbon fibres.

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47

48 **1. Introduction**

49

50 The increasing demand for plastics observed during the past decades, and the subsequent waste accumulation,
51 have emphasized the need to reduce the production of single-use plastic goods and to replace petrochemical-
52 derived polymers with degradable choices, obtained through sustainable productions [1,2]. Furthermore, a

53 major industrial waste is represented by organic solvents, which raised significant concerns related to their
54 disposal due to safety and pollution reasons [3–5]. As a consequence, the substitution of fossil-based products
55 with eco-friendly choices has become an active field of research and one of the main aims of the Green
56 Chemistry [6–8]. For this reason, environmental-friendly solvents and bioplastics are being studied and
57 developed as sustainable replacements for a transition towards a circular economy [9]. In this regard, a
58 sustainable alternative to organic solvents has recently been given by deep eutectic solvents (DES), liquid
59 products obtained through the formation of an eutectic mixture of organic compounds, generally between two
60 and three in number [10–15]. In addition, by exploiting natural low-cost products such as sugars, carboxylic
61 acids, and amino acids, the so-called natural deep eutectic solvents (NADES) have been developed, where the
62 use of choline chloride (CHO) and citric acid (CIT) -based systems has been extensively reported [16–18]. On
63 the other hand, bioplastics are commonly defined as bio-based and/or biodegradable polymers, which can be
64 broadly divided into (i) polymers that are both bio-based and biodegradable, (ii) polymers that are only bio-
65 based, (iii) and polymers that are only biodegradable [19]. The first group comprises polysaccharides such as
66 starch and cellulose but also lignocellulosic fibres, materials that attracted a great scientific and industrial
67 interest mostly associated with their intrinsic safety [20–26]. Therefore, they have been exploited for
68 packaging, food, environmental, pharmaceutical, and medical applications [27–35].

69 In this frame, starch enzymatic conversion products, beta cyclodextrins (β CDs) are cyclic truncated-cone-
70 shaped molecules composed of seven α -(1,4)-linked glucopyranose units surrounding a slightly lipophilic inner
71 cavity [36,37]. The presence of this peculiar domain enables the latter to accommodate guest molecules
72 through the formation of inclusion complexes [38–41]. In addition, the hydroxyl functionalities owned by
73 β CD, make them suitable building blocks for the synthesis of different polymer structures [42–44]. Both water-
74 insoluble (cross-linked) and water-soluble (linear or hyper-branched) polymers have been developed by
75 exploiting proper synthetic conditions and suitable cross-linkers, such as organic carbonates, dianhydrides,
76 poly-carboxylic acids, diisocyanates, and diglycidyl ethers [45–47]. Besides, owing to their tuneable synthesis,
77 good chemical stability, and biocompatibility, β CD-based polymers have been widely applied as drug carriers,
78 gas traps, fillers, photo-stabilizers, adsorbents, and fire-retardant agents [48–54]. However, the use of organic
79 solvents or toxic reactants has been often reported as a synthetic approach. For this reason, achieving the same
80 goal with green alternatives would lead to more sustainable and eco-friendly processes suitable for large-scale
81 productions, improving this class of materials [55–59]. The use of β CD in combination with NADES systems
82 has been already reported for extracting, encapsulating, and catalytic scopes, while the synthesis of β CD-based
83 polymers has been recently reported by our group, using CHO/CIT-based NADES as solvent/reactive media
84 [60–69]. The peculiarity of this functional water-soluble product is that it can be turned into a cross-linked,
85 water-insoluble product, via facile thermal treatment. This feature allows the processing of the aforementioned
86 polymer into specific morphologies e.g., fibres or particles, starting from its water solutions, before securing
87 the chosen form via cross-linking, for further applications.

88 In this context, electrospinning is a facile, cost-effective, and flexible approach that allows the production of
89 fibres at micron, submicron and nano-scale, from an electrically charged jet of polymer solutions or melts [70].

90 Starting from the last decades, the development of this technique has now consolidated its role in the processing
91 of a rich variety of polymers mostly for filtration, biosensors, drug delivery, tissue engineering, and wound
92 dressings applications [71–74]. However, organic solvents are often required to obtain polymer solutions and
93 this represents a limitation for many industrial productions due to environmental and safety regulations [75–
94 78]. With the above in mind, the possibility to obtain fibrous mats via electrospinning from NADES-derived
95 β CD-based polymer would allow to obtain a novel fibrous system, avoiding the use of any organic solvent,
96 fossil-derived polymer, or toxic compound, describing a sustainable process.

97 Furthermore, bio-derived products such as wood, nutshells, and starch, have been also studied as a precursor
98 for the production of activated carbons, materials characterised by a porous structure with surface area ranging
99 from 500 to more than 2000 m²/g [79–83]. Thanks to this feature, they display good adsorption capability
100 towards a wide variety of organic and inorganic pollutants, while the choice of the precursor represents a key
101 factor to obtain a good surface development and good structural characteristics [84–86].

102 Besides, the development of high-performance energy storage systems, observed as a consequence of the
103 widespread application of electric devices and vehicles, has required power sources with high power densities,
104 long cyclic life, and enhanced safety [87,88]. In particular, great interest has been given to rechargeable
105 lithium-based batteries and supercapacitors, where carbon materials have been widely employed in the
106 electrodes, as conductive additives, and as substrates for supporting metal oxides, due to their electrical
107 conductivities, surface areas, and chemical stability [89]. In this frame, carbon nanofibers displayed several
108 advantages, if compared to other carbon materials, thanks to the high aspect ratio which enables the formation
109 of a conductive network [90,91].

110 Approximately 90% of the commercial carbon fibres are produced from polyacrylonitrile-based systems or
111 mesophase pitch, and due to their excellent mechanical properties and thermal stability, they have been
112 extensively applied to reinforce polymer-based composites for aerospace, automobile, sporting applications,
113 and construction industries [91–94]. However, the petrochemical nature of the precursors and the costs
114 associated with the production process, represent a limit on the availability of these goods.

115 In the awareness that both granular and fibrous β CD-based polymers have been reported to be effective
116 microporous carbons precursors [95–97], in this work, a water-soluble β CD-based polymer, synthesized using
117 a functional CHO/CIT-based NADES, was studied to produce novel environmentally-friendly bio-based
118 fibres. These fibres were obtained via electrospinning technique utilizing sustainable processing conditions.
119 Furthermore, the possibility to turn the so-obtained water-soluble polymer fibres into water-insoluble ones
120 without altering the morphology, via facile thermal treatment, was evaluated. Eventually, the pyrolysis of the
121 spun substrates was screened as an approach to produce fibrous carbons, while the pyrolysis of fibres obtained
122 from blends of β CD-based polymer and polyethylene oxide, added as a pore initiation agent, was evaluated to
123 modulate the porosities of the resulting carbon fibres.

124

125 **2. Experimental**

126 **2.1 Materials**

127

128 β CD were provided by Roquette Freres (Lestrem, France), while citric acid (CIT), choline chloride (CHO),
129 sodium hypophosphite monohydrate (SHP) polyethylene oxide (PEO, Mw 600,000 Da), sodium hydroxide
130 (NaOH), hydrochloric acid (HCl), oxalic acid, orthophosphoric acid, acetonitrile, and atenolol were purchased
131 from Sigma-Aldrich (Darmstadt, Germany). β CD and CHO were dried in an oven at 75°C up to constant
132 weight before use.

133

134 **2.2 Polymer synthesis**

135

136 The synthesis of the polymer was carried out with a procedure previously developed by our research group
137 [69]. Firstly, the NADES was prepared by mixing in a round-bottom flask, 2.66 g of dry CHO and 7.34 g of
138 dry CIT. The physical mixture was heated up at 140°C until a clear and transparent liquid was observed.
139 Afterwards, by keeping the NADES at 140°C, 1.00 g of β CD and 0.10 g of SHP, as a catalyst, were added. A
140 transparent liquid was obtained after 20 to 30 seconds of stirring under a vacuum using a diaphragm pump.
141 Subsequently, the flask was cooled down to 110°C, at atmospheric pressure. The reaction was then carried out
142 at 110°C under a vacuum for 6 hours. At the end of the reaction, the product appeared as a yellow to light
143 brown bulk solid. The polymer was further recovered from the round-bottom flask by crushing it with a spatula.
144 Then it was solubilized in distilled water at room temperature and purified by ultrafiltration (cut off 10 kDa)
145 to separate the actual polymer from non-reacted β CD, reactants, and oligomers. The polymer solution was then
146 recovered from the ultrafiltration cell and subsequently freeze-dried, obtaining a pale-yellow powder. The
147 average molecular weight of the resulting polymer was 19 kDa [69].

148

149 **2.3 Characterisation**

150

151 Thermogravimetric analyses (TGA) were carried out using a TA Instruments Q500 TGA (New Castle, DE,
152 USA), from 50°C to 700°C, under nitrogen flow, with a heating rate of 10°C/min.

153 A Perkin Elmer Spectrum 100 FT-IR Spectrometer (Waltham, MA, USA) equipped with a Universal ATR
154 Sampling Accessory was used for FTIR-ATR (Attenuated Total Reflection) characterisation. All spectra were
155 collected in the wavenumber range of 650-4000 cm^{-1} , at room temperature, with a resolution of 4 cm^{-1} and 8
156 scans/spectrum.

157 The chemical composition of the samples was studied using a Thermo Fisher FlashEA 1112 Series elemental
158 analyser (Waltham, MA, USA).

159 A Malvern Zetasizer Nano-ZS (Malvern, United Kingdom) was used to measure the zeta (ζ)-potential. All the
160 tests were performed using distilled water at room temperature.

161 The morphology of the samples was studied using scanning electron microscopy (SEM). The images were
162 acquired with a Tescan VEGA 3 (Brno, Czech Republic) using secondary electrons and 15 kV accelerating
163 voltage. Prior to SEM characterisation, the samples were ion-coated with gold using a Baltec SCD 050 sputter

164 coater (Pfäffikon, Switzerland) for 40 seconds, under vacuum, at 60 mA. Furthermore, for the observation of
165 the pyrolysed sample's surfaces, a FE-SEM Tescan S9000G (Brno, Czech Republic) was employed, using
166 secondary electrons, 15 kV accelerating voltage, and ultrahigh-resolution conditions. ImageJ software was
167 used to evaluate the fibre's diameters.

168

169 **2.4 Processing**

170

171 A self-made electrospinning apparatus was used to process all the solutions. The deposition was carried out at
172 room temperature and relative humidity comprised between 30% and 45%. A working distance of 15 cm, 30
173 kV field strength, and 1.2 mL/hour flow were set to spin the β CD-based polymers, while a working distance
174 of 15 cm, 20 kV field strength, and 0.3 mL/hour were set to process the blends of β CD-based polymer/PEO.
175 A Linari NanoTech Easy Drum (Pisa, Italy) rotary system equipped with an aluminium cylinder was used as
176 the collector, with a rotation speed of 75 rpm; a gauge 18 nozzle was employed.

177

178 **2.5 Curing and pyrolysis**

179

180 A Lenton 1200 tubular furnace was used to carry out both the curing and pyrolysis treatments. In the first case,
181 the samples were kept at 180°C for 30 minutes, under 100 NI/h nitrogen flow, while in the second case they
182 were heated from room temperature to 700°C, under nitrogen flow of 100 NI/h, with a heating rate of 10°C/
183 min. In both cases, the samples were maintained under nitrogen flow until room temperature was restored,
184 after the thermal treatment.

185

186 **2.6 Solubility test**

187

188 For each sample, 50 mg of polymer mat were placed in a 5 mL Eppendorf tube, and then 5 mL of deionized
189 water were added. After 24 hours at room temperature, the solution was separated from the mat via
190 centrifugation, and the latter was dried in an oven at 60°C up to constant weight. The test was carried out in
191 triplicate. The soluble fraction was calculated as follows,

192

193

$$194 \quad \text{Soluble fraction (\%)} = \left(\frac{SMP_{before} - SMP_{after}}{SMP_{before}} \right) * 100$$

195

196

(1)

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198 where SMP_{before} and SMP_{after} represent the weights of the mat (mg) before and after the test, respectively.

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2.7 Potentiometric titration

The content of free carboxylic groups present within the polymer products was determined via potentiometric titration, according to the procedure described by Soto et al., with slight modifications [98]. A 0.10M NaOH solution was used as a titrant, pre-standardized with a 25 mM oxalic acid solution. The titration was carried out by adding 0.1 mL of the titrant each step, using a volumetric burette, into the sample solution which was kept under gentle stirring and at room temperature. Titrant additions were performed at 60 seconds intervals, to allow equilibrium to be achieved. Besides, pH values were continuously measured and recorded, using a pH meter, after each addition, until the pH of 12 was reached. Subsequently, the titration curve of pH versus titrant volume was generated and the curve's inflection point was found via the second derivative approach. The volume of NaOH consumed at the inflection point was applied to the following equation, to calculate the milliequivalents of acidity per 100 g of sample:

$$\frac{m_{eq} \text{ of acidity}}{100 \text{ g sample}} = \frac{(V_s - V_b) * C_{NaOH} * 100}{m_s} \quad (2)$$

where m_{eq} are milliequivalents, V_s and V_b are the volumes of NaOH consumed by the sample and the blank (β -CD was considered as a blank), whereas C_{NaOH} is the concentration of NaOH in mol/L, and m_s is the mass of the sample. The potentiometric titrations were performed in duplicate.

2.8 Probe molecules adsorption tests and HPLC-UV/Vis detection

Batch adsorption tests were performed starting from 25 mL of 1 and 10 mg/L atenolol water solutions, at room temperature. Calibration curves were constructed before the sample analysis, from 0.2 to 1 mg/L for the test performed at 1 mg/L and from 1 to 10 mg/L for the tests carried out at 10 mg/L. The adsorption tests were performed in triplicate by adding, in separate tests, 25 mg of the cross-linked mat or of the carbon fibres to probe solutions. All the dispersions were continuously stirred at room temperature with an orbital shaker. At fixed intervals, the concentration of atenolol was measured via HPLC-UV/Vis technique, by using a Dionex (Sunnyvale, CS, USA) consisting of a P680 pump coupled with a UVD170U detector. Separation was achieved on a Kinetex® C18 (150 x 4,6 mm, 5 μ m). The mobile phase consisted of 0.1% orthophosphoric acid in water and acetonitrile in the ratio of 90:10 v/v. The mobile phase was filtered through a 0.45 μ m nylon filter and degassed prior to use. The quantification of atenolol was performed at 230 nm while the run time for the assay was 6.5 minutes at 1mL/min. The retention time for atenolol was 4.7 min.

238

239 **3. Results and discussion**

240 **3.1 Polymer characterisation**

241

242 The first step of the work was focused on synthesizing a β CD-based polymer, exploiting a CHO/CIT-based
243 NADES as a solvent, and at the same time, as a reactive media system. This was possible thanks to the
244 capability of (i) CIT to act as the cross-linker and (ii) CHO as the functional molecule, as recently described
245 by our group [69]. The reported mechanism involves the formation of anhydride intermediates (Figure 1A),
246 which can easily be attacked by the hydroxyl groups of either β CD or CHO, causing the formation of ester
247 bonds. The formation of a bridge between β CD determines the growth of the polymer chain, while a bridge
248 between β CD and CHO forms a positively charged pendant, as reported in Figure 1B.

249 The presence of a product after the purification step carried out via ultrafiltration technique with a 10k Da cut-
250 off membrane, demonstrated the occurrence of the polymerization reaction. The obtained polymer,
251 approximately 25 wt. % of the non-purified one was subsequently characterised to also assess the presence of
252 positively charged pendants imparted by CHO molecules. FTIR-ATR and elemental analysis measurements
253 were performed for this purpose. Figure 2A reports the FTIR-ATR spectra of the polymer product. The peak
254 centred at 1720 cm^{-1} and the shoulder at 1178 cm^{-1} , supported the mechanism behind the formation of ester
255 bridges and the presence of free carboxyl functions, imparted by CIT molecules. In addition, the presence of a
256 peak centred at approximately 1478 cm^{-1} , typical of quaternary ammonium functions, represents a starting
257 proof of the presence of grafted ammonium groups (see the spectrum of CHO in Figure 2E). The elemental
258 analysis of the polymer product gave a nitrogen content of $2.28\pm 0.10\text{ wt. \%}$, as a confirmation of the reactions
259 involving CHO molecules.

260

261 **3.2 Electrospinning**

262

263 The possibility to produce fibres and mats, with high surface-to-volume ratio and controllable structures and
264 morphologies, is a unique feature offered by the electrospinning technique. Nevertheless, an optimization of
265 the processing parameters is required to get fibres without defects. The parameter that most influences the
266 process is the concentration of the polymer solution and, therefore, its viscosity, reflecting the entanglements
267 generated between the polymer chains and proportional to the molecular weight of the latter. Consequently,
268 the work was firstly focused on screening the optimal polymer concentration, necessary to obtain a good
269 deposition, lack of defects on the obtained fibrous mats, and absence of difficulties such as clogging of the
270 nozzle, during the processing step. Different amounts of polymer powder were solubilized in deionized water
271 at room temperature, with the purpose to obtain distinct solutions with concentrations ranging from 50 wt. %
272 to 70 wt. %, at increasing amounts of approximately 2 wt. % one to the next. After complete solubilization,
273 the electro-spinnability of each solution was evaluated.

274 Figure 3 shows the results of the screening. At a concentration of 62.50 wt. % (Figure 3A, 3B) the presence of
 275 beads and short split fibres, was proof that the polymer concentration was still low. On the contrary, the
 276 clogging of the nozzle and the low deposition yield were observed while spinning the solutions at 66.67 wt. %
 277 (Figure 3G, 3H), and suggested that in that case, the concentration exceeded the optimum condition.
 278 Eventually, the best processing and produced mats were observed from polymer solutions at 64.52 wt. %
 279 (Figure 3D, 3E). In this case, the absence of beads and well-defined fibres with a mean diameter of 0.79 ± 0.19
 280 μm were observed as the product. Besides, at increasing polymer concentrations, an increase in the mean
 281 diameters was observed accordingly (by comparing Figure 3C, 3F, and 3I), also associated with more
 282 polydisperse systems.

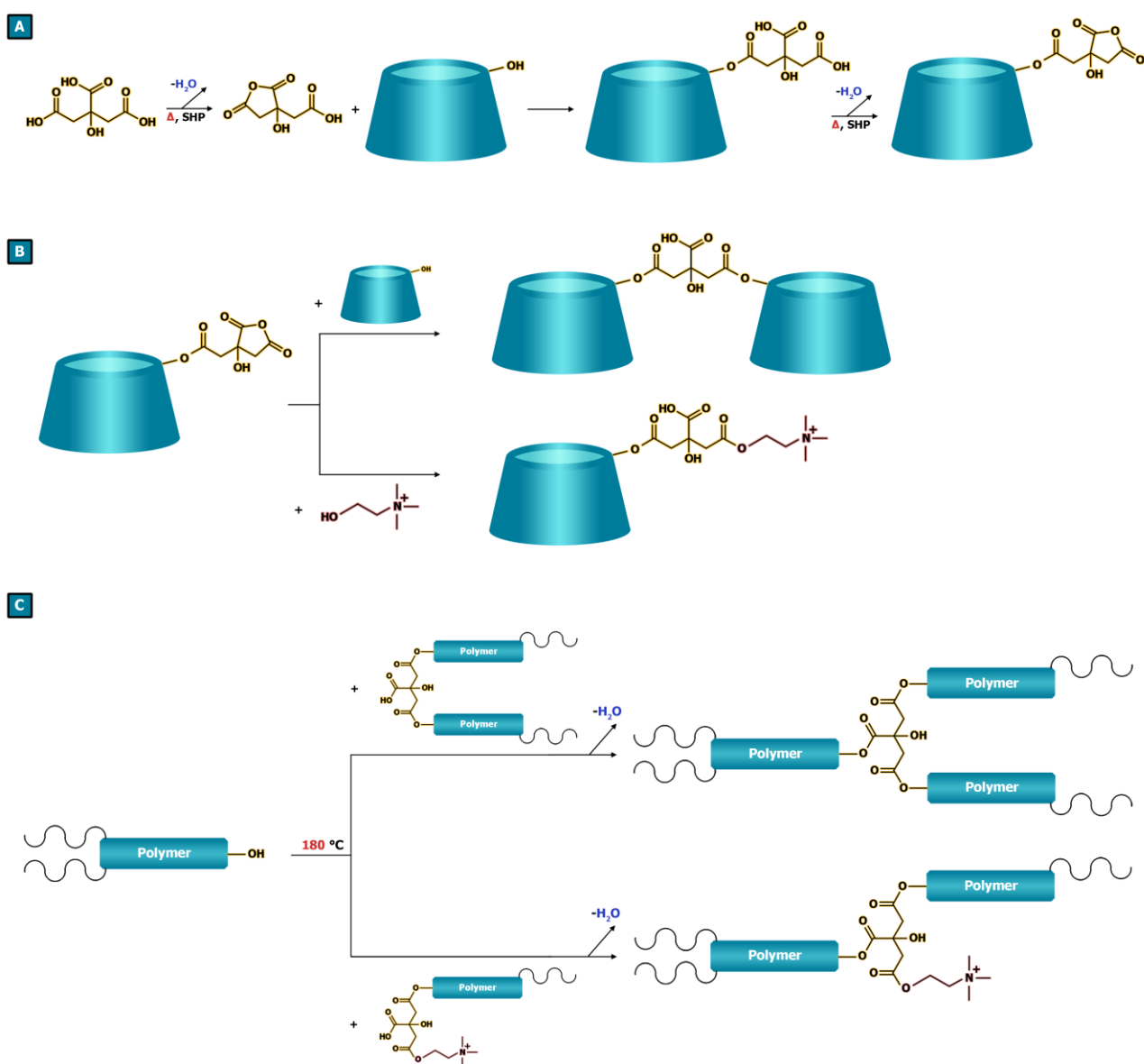


Figure 1 Reactions occurring during the synthesis of the polymer: (A) Formation of anhydride intermediates, (B) anhydride ring-opening reactions giving bridges between βCDs and bridges between βCD and CHO molecules. (C) Reactions occurring during the curing process.

283 3.3 Fibre's curing

284

285 After demonstrating the possibility to obtain fibrous mats from the electrospinning of the β CD-based polymer
286 water solutions, the capability to cross-link their structure without altering the fibrous morphology, thus
287 obtaining insoluble products, was evaluated. The fibres obtained from solutions at 64.52 wt. % were chosen to
288 perform this study. At first, the polymer was analysed via TGA to study its thermal stability. Figure 2F (solid)
289 shows that the fibres resulted thermally stable up to approximately 130°C, while the degradation took place in
290 a three-step process occurring roughly between 150°C and 400°C, giving a stable carbon residue at 700°C,
291 corresponding approximately to 18% of the initial weight. However, the weight loss phenomenon centred
292 approximately at 180°C, evidenced by the derivative curve (Figure 2G, solid), has been attributed to the loss
293 of water, as a product of the esterification reactions, causing the curing of the polymer structure, as reported
294 in Figure 1C [69]. For this reason, 180°C was chosen as the temperature to perform the cross-linking process.
295 Consequently, the weight loss associated with the esterification reactions was no longer evident after the
296 thermal treatment (Figure 2G, dashed), confirming the hypothesized mechanism. Potentiometric titrations were
297 exploited to quantify the number of free carboxylic groups present in the polymer before and after the thermal
298 treatment, as further evidence of the occurrence of the esterification reactions resulting in cross-linking of the
299 polymer. The results are expressed as milliequivalents of acidity per 100 g of the tested sample, calculated
300 according to Eqn. 2, thus proportional to the number of carboxylic groups displayed by each sample. As a

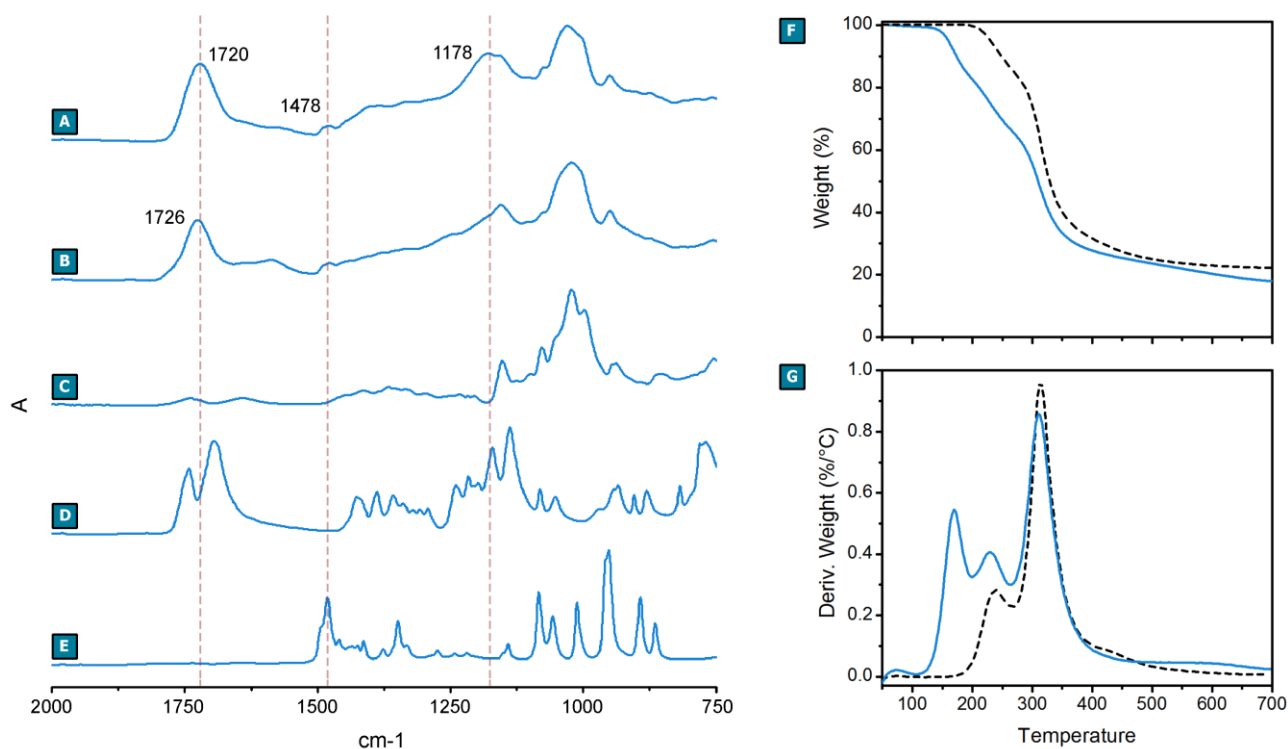


Figure 2 FTIR-ATR spectrum of water-soluble polymer (A) cured polymer (B), β CD (C), CIT (D), and (E) CHO. Water soluble polymer (solid) and cured polymer (dashed) TGA (F) and (G) DTGA curves.

301 result, the polymer before the thermal treatment displayed 462 ± 3 m_{eq} of acidity, whereas the polymer after
 302 thermal treatment was characterized by 124 ± 2 m_{eq} of acidity. The results obtained are consistent with the
 303 hypothesized mechanism (Figure 1), since the esterification reactions taking place during the curing of the mat
 304 are associated with a decrease in the number of free carboxyl groups. Eventually, after curing, the polymer
 305 resulted stable up to 200°C, while a carbon residue, corresponding approximately to 22% of the initial weight,
 306 was observed as the result of a two-step degradation process.

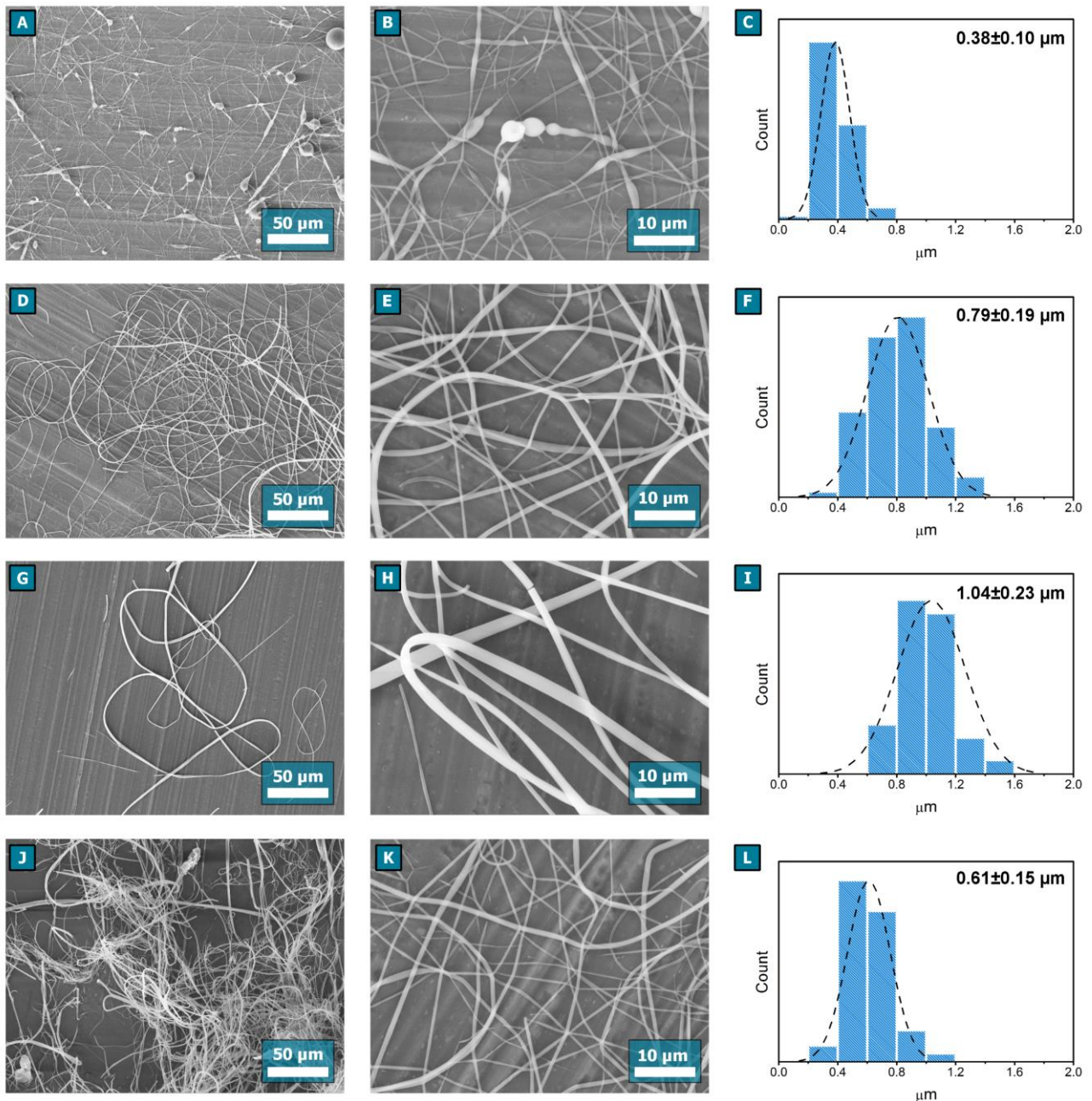


Figure 3 SEM images and diameters distributions of spun polymer fibres obtained from (A, B, and C) 62.50 wt. %, (D, E, and F) from 64.52 wt. %, and (G, H, and I) from 66.67 wt. % water solutions. (J, K, L) SEM images and diameters distributions of fibres obtained from 64.52 wt. % polymer solution, after thermal treatment at 180°C.

307 The morphology of the cured samples was investigated, and the results obtained (Figure 3J, 3K) clearly showed
308 distinct fibrous mats, confirming the retention of the morphology obtained via electrospinning, after the
309 thermal treatment. Because of the curing, a slight decrease in the fibre's diameters was detected, being the
310 latter characterised by an average value of $0.61\pm 0.15\ \mu\text{m}$. Eventually, water solubility tests were carried out
311 as a further evaluation of the studied thermal curing. The mats were dipped in deionized water at room
312 temperature and recovered via centrifugation after 24 hours. After being dried up to constant weight, the
313 soluble fraction was calculated according to Eqn. 1 and resulted in equal to $21.6\pm 1.1\%$. Hence, approximately
314 the 80 wt. % of the starting material was recovered. This result further confirmed the occurrence of cross-
315 linking reactions, giving a water-insoluble polymer structure, while the observed polymer loss was related to
316 the presence of polymer chains that did not undergo a complete cross-linking, and to hydrolytic mechanisms
317 taking place during the test. Also, the cross-linked polymer displayed a higher nitrogen content (2.92 ± 0.01 wt.
318 %) than the water-soluble one, caused by the water released as a condensation product. In addition, by
319 analysing the polymer via ζ -potential analysis, a positive value of 13.1 ± 1.3 mV was observed, imparted by the
320 quaternary ammonium pendants related to bound CHO molecules. This feature allows the polymer to display
321 electrostatic interactions towards negatively charged target molecules for e.g. adsorption or release
322 applications.

323

324 **3.4 Fibre's pyrolysis**

325

326 In light of the significant amount of carbon residue observed as the product of the polymer thermal degradation,
327 the electrospun β CD-based polymer mats were studied as a novel precursor to obtaining carbon fibres. Again,
328 the fibres obtained from solutions at 64.52 wt. % were chosen for this purpose. The pyrolysis of the polymer
329 mat was performed either (i) at ambient pressure under a 100 NL/h nitrogen flow, or (ii) at 1 mbar pressure, via
330 a vacuum line coupled to a rotary vane pump. In both cases, 700°C was chosen as the temperature to produce
331 the carbon product. After the thermal treatments, the samples were studied via SEM and FE-SEM, to
332 characterise their morphology and surface features, respectively. As reported in Figure 4, both approaches used
333 led to samples displaying fibrous morphology, characterised by similar mean diameters of $0.49\pm 0.10\ \mu\text{m}$ in
334 the case of nitrogen atmosphere, and $0.46\pm 0.14\ \mu\text{m}$ in the case of vacuum conditions. However, the FE-SEM
335 images (Figure 4C, 4G) showed that the samples appeared to be characterised by slightly different surface
336 features. In the first case (nitrogen flow, Figure 4C), an uneven surface characterised by roughness comprised
337 between a few nanometres to 50 nm, was detected. On the other hand, in the second case (vacuum, Figure 4G),
338 the sample appeared to be characterised by flat surfaces, where the presence of porosity was not observed.
339 However, considering that the 80% weight loss observed because of the thermal degradation (Figure 2F) is
340 associated to only a 20% decrease of the fibre's diameters after the pyrolysis process (Figure 3J, 3K, 3L), an
341 overall hollow porous structure characterizing the carbon product, can be hypothesized.

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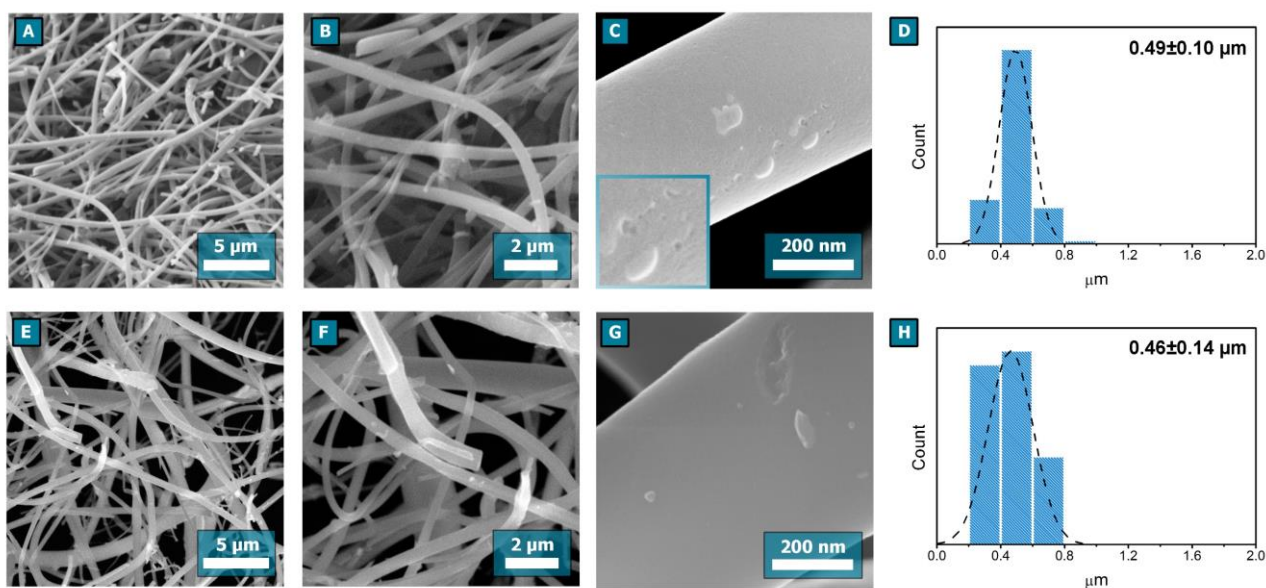


Figure 4 SEM, FE-SEM, and diameter distributions images of carbons obtained from the pyrolysis of fibrous mats, spun from a 64.50 wt. % β CD-based polymer. Thermal treatment carried out under nitrogen flow (A, B, C, D), and thermal treatment carried out under vacuum (E, F, G, H).

343 3.5 Porous carbons

344

345 Once assessed the capability of the reported spun mats to be exploited as suitable substrates to produce carbon
 346 sub-micrometric fibres, the last step of the work was focused on validating the possibility to tune their
 347 porosities, observed as the result of the thermal treatment. One popular approach to preparing porous carbons
 348 is to blend non-char polymers with char-forming ones, exploiting the former as pore initiation agents during
 349 the pyrolysis step. To this end, PEO has often been reported as a suitable choice [99–101]. Hence, solutions of
 350 polymer blends composed of the reported β CD-based polymer and PEO were prepared and subsequently

Blend	wt. %		Fibre's diameters (μm)	Carbon pore diameters (nm)
	β CD-based polymer	PEO		
1	0.06	0.06	0.58 ± 0.07	\
2	0.09	0.06	0.61 ± 0.12	\
3	0.12	0.06	1.02 ± 0.30	\
4	0.24	0.06	1.43 ± 0.91	24 ± 8
5	0.36	0.06	1.87 ± 0.26	15 ± 6
6	0.48	0.06	1.81 ± 0.63	13 ± 4

Table 1. β CD-based polymer/PEO blends processed via electrospinning, resulting fibre's diameters, and carbon pore size distribution.

351 electrospun. Firstly, the electrospinning parameters were optimized to get fibres from PEO water solutions.
352 Further, the deposition of well-defined fibres characterised by mean diameters of $0.46 \pm 0.07 \mu\text{m}$ was observed

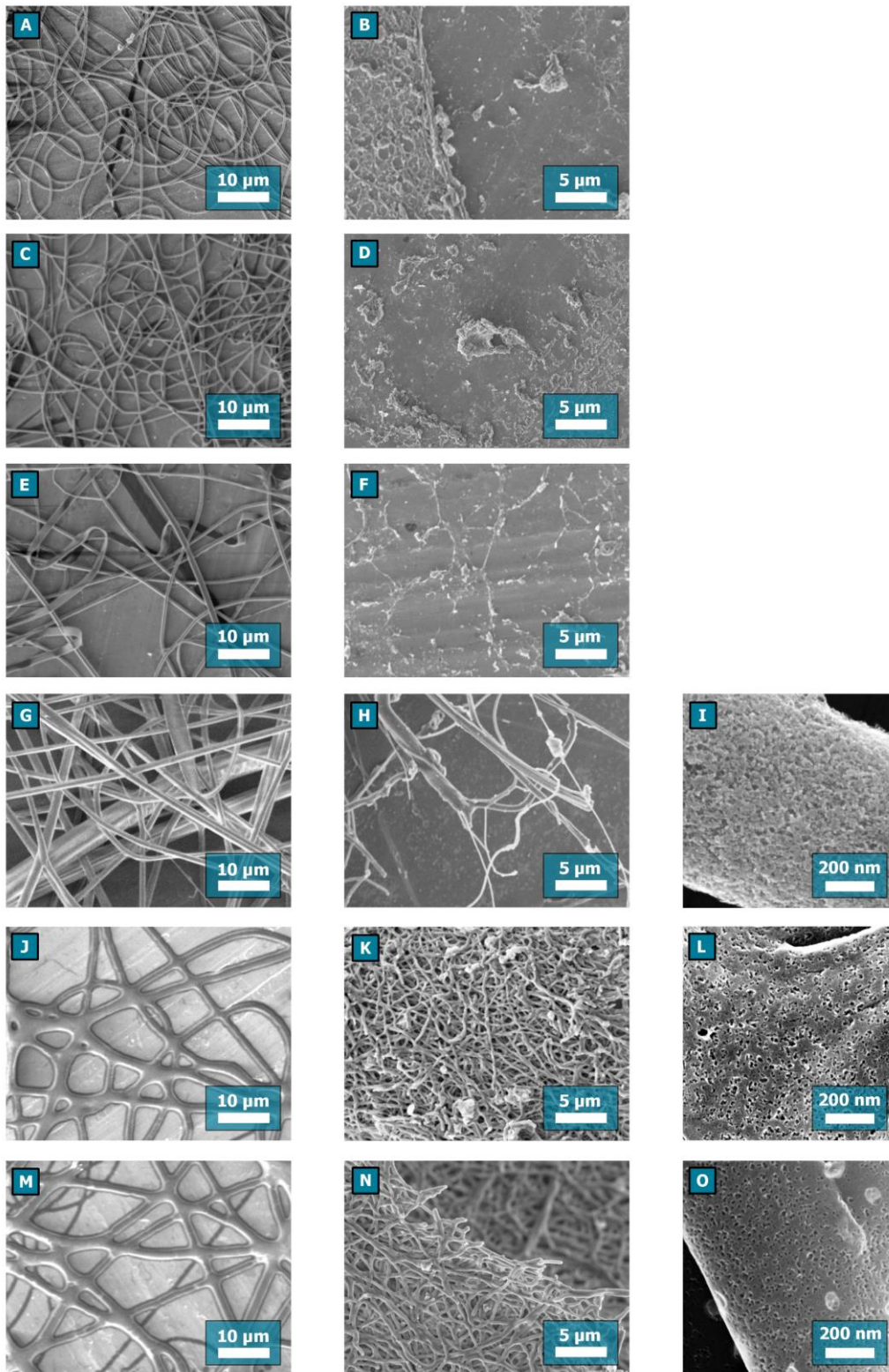


Figure 5 SEM images of spun mats (first column), resulting carbons (second column), and FE-SEM of carbon porosity (third column) obtained from: Blend 1 (A, B), Blend 2 (C, D), Blend 3 (E, F), Blend 4 (G, H, I), Blend 5 (J, K, L), Blend 6 (M, N, O).

353 from 5.66 wt. % solutions. Afterwards, the electro-spinnability of the different β CD-based polymer/PEO
354 blends was tested (Table 1). As shown in Figure 5, the deposition of fibres was observed from the processing
355 of all the blends studied. Moreover, an increase in the average fibre diameters was detected, proportional to
356 the increasing amount of β CD-based polymer in the blend. After the electrospinning, all the mats were
357 pyrolyzed under nitrogen flow, as previously described, and the resulting carbon products were further
358 characterised to assess the retention of the fibrous morphology and the presence of any porosity. The pyrolysis
359 of the mats obtained from Blend 1 and Blend 2 did not lead to fibrous products, probably due to the lower
360 amount of β CD-based polymer compared to that of PEO. In these cases, the amount of char-forming polymer
361 resulted too low to allow the fibrous morphology to be retained during the volatilization of PEO. Further, the
362 presence of small fibrous domains is apparent in Figure 5F (Blend 3), suggesting that the increasing amount
363 of β CD-based polymer might result beneficial to obtain fibrous products. As proof, from Blend 4, Blend 5,
364 and Blend 6, fibrous carbons were obtained as pyrolysis products. The carbon fibres obtained from Blend 4
365 were characterised by a mean diameter of $1.23\pm 0.56\ \mu\text{m}$, with a diameter decrease of approximately 15%, if
366 compared to the spun mat. A decrease of the diameters of approximately 55% was observed instead from Blend
367 5 and Blend 6, at increasing β CD-based polymer amount, being the carbon fibres characterised by a mean
368 diameter of $0.63\pm 0.15\ \mu\text{m}$ and $0.76\pm 0.18\ \mu\text{m}$, respectively. This behaviour was related to the electrospinning
369 process; as reported in Figure 5J and Figure 5M, the fibres obtained were not well-defined, but coalescence
370 phenomena took place once they reached the collector. This feature is commonly related to a deposition carried
371 out in a non-optimal condition, in which a fraction of solvent (distilled water), is still present in the fibres when
372 they reach the collector (in optimal conditions, the solvent evaporates completely before the fibres reach the
373 collector). For this reason, the fibres appear stick one to each other, characterised by larger diameters, and
374 displaying a higher diameter decrease during the pyrolysis. Nevertheless, after a fine evaluation of the so-
375 obtained carbon products, the presence of porosity was detected on the surfaces of the studied carbon fibres,
376 suggesting how the solvent residues observed during the deposition did not alter the pore formation. From the
377 pyrolysis of Blend 4 fibres, pores with an average diameter of $24\pm 8\ \text{nm}$ were detected, while from Blend 5 and
378 Blend 6, pores with diameters of $15\pm 6\ \text{nm}$ and $13\pm 4\ \text{nm}$ were observed, respectively. Eventually, from the
379 evaluation of the pores distribution, their quantities and dimensions resulted proportional to the ratio β CD-
380 based polymer/PEO, as a confirmation of the pore-generating mechanism, the lower the amount of pore
381 initiation agent the lower the resulting porosity.

382

383 **3.5 Evaluation of adsorption performances**

384

385 The cross-linked mat and the carbon fibres obtained without employing PEO, were further screened as suitable
386 adsorbents for the removal of pollutants from contaminated water. The test was carried out by simulating water
387 samples containing pharmaceutical products, considered emerging pollutants [102,103]. Consequently,
388 atenolol, a beta-blocker medication used mainly to treat cardiovascular diseases, was chosen as the probe
389 molecule [104]. The tests were carried out from 25 mL of a 10 mg/L (Figure 6A) and a 1 mg/L (Figure 6B)

390 atenolol distilled water solutions which were placed in contact with 25 mg of adsorbent. Subsequently, the
391 concentration of atenolol was monitored at fixed time intervals. As a result, the crosslinked mat displayed
392 higher adsorption performances ($60.2\pm 0.3\%$ from 10 mg/L, and $66.5\pm 0.7\%$ from 1 mg/L) if compared to the
393 carbon fibers ($17.1\pm 1.7\%$ from 10 mg/L, and $42.4\pm 2.6\%$ from 1 mg/L). Further, the cross-linked mat showed
394 a fast kinetics, reaching a plateau after approximately 30 minutes of contact between the adsorbent and the
395 solution. Thereby, the adsorption performances observed can be related to the capability of the cross-linked
396 mat to form stronger electrostatic interaction with the molecules of atenolol, compared to the carbon fibres,
397 and to the possibility to generate host-guest complexes by exploiting the presence of the cavities of β CD
398 composing the polymer chains [105].
399
400

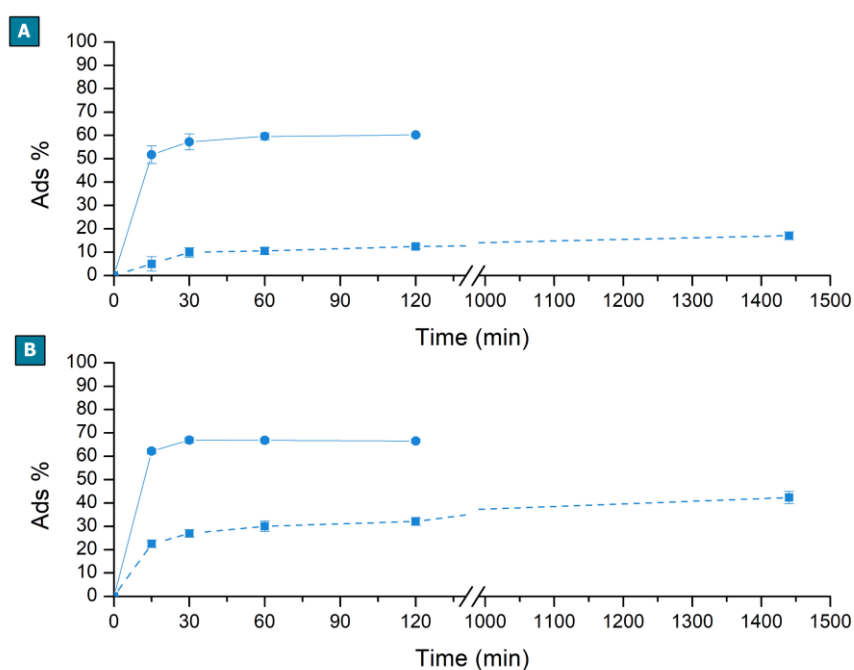


Figure 6 Atenolol adsorption tests. Adsorption profiles of cross-linked mat (solid), carbon fibres (dashed). (A) Test performed from 10 mg/L atenolol solution, and (B) test performed from 1 mg/L atenolol solution.

4. Conclusions

401
402
403 Citric acid/choline chloride NADES-derived beta cyclodextrin (β CD)-based polymers demonstrated to be
404 suitable materials to obtain the deposition of bio-based fibres via electrospinning, without the use of any
405 synthetic carrier polymer. Moreover, as a result of the intrinsic water solubility of the chosen polymers, the
406 process was carried out using water as the unique solvent, thus exploiting a sustainable approach. An optimum
407 condition to obtain the deposition of well-defined fibres, with diameters of $0.79\pm 0.19\ \mu\text{m}$, was identified using
408 64.52 wt. % polymer solution. Subsequently, to overcome the intrinsic solubility of the obtained mats, the
409 fibres were thermally treated via a one-step process, exploiting the presence of a residual reactivity
410 characterizing the polymer. Thermal curing carried out at 180°C was demonstrated (i) to trigger condensation

411 reactions between the polymer chains, giving cross-linked, water-insoluble networks, and (ii) to retain the
412 initial fibrous morphology, obtaining water-insoluble sub-micrometric fibres. In addition, the mats were
413 screened as a bio-derived precursor to produce fibrous carbon materials. The pyrolysis of the spun products at
414 700°C, in both nitrogen flow and vacuum conditions, led to carbon materials that displayed fibrous features
415 and fibre diameters lower than 500 nm. Furthermore, the introduction of a pore initiation agent was evaluated
416 as an approach to tune the porosity of the previously described fibrous carbons. Different blends of β CD-based
417 polymer and polyethylene oxide (PEO) were prepared and subsequently spun into fibres. The ratio between
418 β CD-based polymer and (PEO) resulted to be a key factor to get the retention of the morphology after the
419 pyrolysis, and the generation of pores. Porous carbon fibres, with pore size distribution proportional to the
420 amount of PEO content and comprised between 13 nm and 24 nm, were obtained. Eventually, encouraging
421 results were obtained by applying both the cross-linked mats and the carbon fibres as suitable adsorbents for
422 the removal of pharmaceuticals, as emerging pollutants, in polluted waters. The synthesis, processing, curing,
423 and thermal treatment chosen for this work constitute an overall sustainable process, suitable to obtain bio-
424 based cross-linked sub-micrometric fibrous mats and carbons, which can be further studied for environmental,
425 catalytic, pharmaceutical, and medical applications.

426

427 **Author contributions**

428

429 Claudio Cecone: conceptualization, methodology, investigation, validation, formal analysis, visualization,
430 writing - original draft, writing - review & editing. Gjylje Hoti: methodology, investigation, validation, writing
431 - review & editing. Fabrizio Caldera: supervision, methodology, writing - review & editing. Marco Zanetti:
432 supervision, methodology, writing - review & editing. Francesco Trotta: supervision, project administration,
433 writing - review & editing. Pierangiola Bracco: supervision, methodology, project administration, writing -
434 review & editing.

435

436 **Declaration of competing interests**

437

438 The authors declare that they have no known competing financial interests or personal relationships
439 that could have appeared to influence the work reported in this paper.

440

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