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Different carbon fibrous morphologies triggered by varying the average diameter of precursor electrospun fibers

E Svinterikos¹, I Zuburtikudis², M Al Marzouqi¹

¹Department of Chemical and Petroleum Engineering, United Arab Emirates University (U.A.E.U), Al Ain, U.A.E

²Department of Chemical Engineering, Abu Dhabi University, Abu Dhabi, U.A.E.

E-mail: ioannis.zuburtikudis@adu.ac.ae

Abstract. Investigation of the factors affecting the carbonization process is very important for the manufacture of desired, on-demand carbon fibrous morphologies. In this work, the effect of the average fiber diameter on the carbonization of precursor polymer fibers into carbon fibers was examined. Three electrospun fibrous mats consisting of a lignin/recycled PET blend with mass ratio of 1/1 and having different average fiber diameter (80, 387 and 781 nm) were prepared. After they were carbonized at 600 °C, it was found that the thicker fibers (387 and 781 nm) yield well-formed carbon fibrous morphologies, with average diameter of the same range as the precursor ones. In contrast, the thinnest nanofibers with an average diameter of 80 nm fuse with each other and lose their fibrous morphology, due to the maximization of heat and mass transfer during the process. These results highlight the decisive role of the nanoscale dimension in processes controlled by heat and mass transfer phenomena, as in the case of carbon fiber manufacture.

1. Introduction

Fibrous carbon materials have attracted the focus of research due to their suitability for various applications including energy storage and the manufacture of composite materials for the automotive industry [1,2]. Carbon nanofibers (CNFs) especially, a form of fibrous carbon with fiber diameters in the nanoscale, are appropriate for processes in which a large surface area plays a key role, such as in adsorption or catalysis. In these cases, attaining the desired nanostructure morphology is very important for the applicability of CNFs. This can be achieved by a careful selection of the precursor materials and a diligent adjustment of the process conditions [3].

Carbon submicron- and nanofibers are typically manufactured through the thermal treatment of precursor polymer fibers [2,3]. A common polymer for this purpose is poly(acrylonitrile) (PAN), especially in applications where the mechanical properties are significant. However, due to the relatively high cost of this petroleum-based polymer, alternative cheaper feedstock or polymers derived from renewable resources have been examined as well. Lignin seems to successfully serve this purpose. This abundant natural polymer is usually obtained as a waste by-product of the paper industry, and it can also be extracted from waste generated from agricultural activities such as pruning [2,4]. Its suitability for producing CNFs is based on its availability, its low cost, its high carbon content (typically >50% per unit mass), and the absence of toxic gases when it is thermally treated [2,4].

The electrospinning technique has been widely used for the fabrication of precursor polymer submicron- and nanofibers [3]. The fiber spinning through this relatively simple technique is



accomplished after a polymer solution flows at a controlled rate through a syringe under the influence of an electrostatic field, which stretches and elongates the jet formed; as the solvent evaporates, fibers are deposited on a metallic collector [5]. The main advantage of this technique is that the fibrous morphology can be tailor-made by easily adjusting the process conditions. Moreover, a wide variety of polymers or polymer blends can be used.

Our attempts to fabricate precursor electrospun fibers from lignin alone were unsuccessful due to the relatively low molecular weight of this polymer [5]. Instead, the use of a binder polymer was necessary. Therefore, it was decided to use recycled poly(ethylene terephthalate) (rPET) for this purpose. This thermoplastic commodity polymer is one of the most commonly used and one of the most recycled plastics worldwide [4], therefore, developing alternative uses will help to confront grave environmental issues. Besides, rPET is a cheap feedstock of large availability and it has a common solvent with lignin (trifluoroacetic acid).

After the preparation of precursor electrospun fibers, their carbonization allows their transformation into carbon fibers. This process is carried out under heating in inert atmosphere at elevated temperatures (typically >600 °C). During carbonization, decomposition reactions occur, volatile gases evolve (such as CO_2 , H_2 , CH_4 and CH_3CH_3), and the final product consists of a mainly amorphous polyaromatic carbon structure [6].

In this work, we report a phenomenon that we repeatedly noticed after carbonizing precursor electrospun fibers of lignin/rPET. The carbon fibrous morphology that is yielded after carbonization depends on the fiber diameter of the precursor fibers, especially when the diameter is reduced in the nanoscale (<100 nm).

2. Experimental part

The kraft lignin used here was purchased from Sigma-Aldrich (#471003, $M_w \sim 10,000$ g/mol, low sulfonate content) and it was used as received. The recycled PET (rPET) was derived from waste water bottles, which were left to dry and were cut into small pieces. For the preparation of the electrospinning solutions, trifluoroacetic acid (99%) purchased from Merck was used. The solutions of lignin/recycled PET were prepared and left under magnetic stirring at room temperature overnight until they were homogeneously dissolved. The electrospinning process was performed in a FUENCE E-sprayer (ES-2000S) apparatus in which the setup has vertical orientation. In order to examine the effect of the average fiber diameter on the morphology of the carbonized fibers, three electrospun mats of different average fiber diameter were prepared, all of them from lignin/rPET with mass ratio 1/1. The three mats had the following average fiber diameter and standard deviation: a) 80 ± 21 nm, b) 387 ± 148 nm, c) 781 ± 284 nm. For simplification, in the following paragraphs only the average fiber diameter will be mentioned for each mat. For these three samples, the electrospinning voltage was kept at 30 kV, the spinning distance at 7.7 cm and the flow rate at 0.1 $\mu\text{L}/\text{min}$. The difference in the average fiber diameter was the result of using different solution concentrations, namely 9% w/v for mat (a), 25% w/v for (b) and 32% w/v for (c).

The electrospun mats were carbonized in a temperature-programmed tubular furnace (Tube Furnace GSL-1500X-50, MTI). Each sample was heated under inert atmosphere (N_2) at a heating rate of 5 °C/min until it reached 600 °C, where it was held for 1h.

The morphology of the electrospun and of the carbonized samples was examined through scanning electron microscopy (SEM) (JEOL Neoscope JCM-5000) after they were gold-coated. Their derivative thermogravimetric curves were recorded using a TA Q500 instrument. Elemental analysis with Energy Dispersive X-Ray Spectroscopy (EDS) was performed using a JEOL JSM-6010PLUS scanning electron microscope.

3. Results and discussion

Repeated attempts to carbonize the precursor submicron- and nanofibers of lignin/rPET revealed that the morphology of the carbonized fibers depends on the average diameter of the precursor fibers. Relatively thicker submicron fibers of average diameter larger than 300 nm, yield well-formed carbon

nanofibrous structures in which the average fiber diameter is of the same range as of the precursor fibers (figure 1).

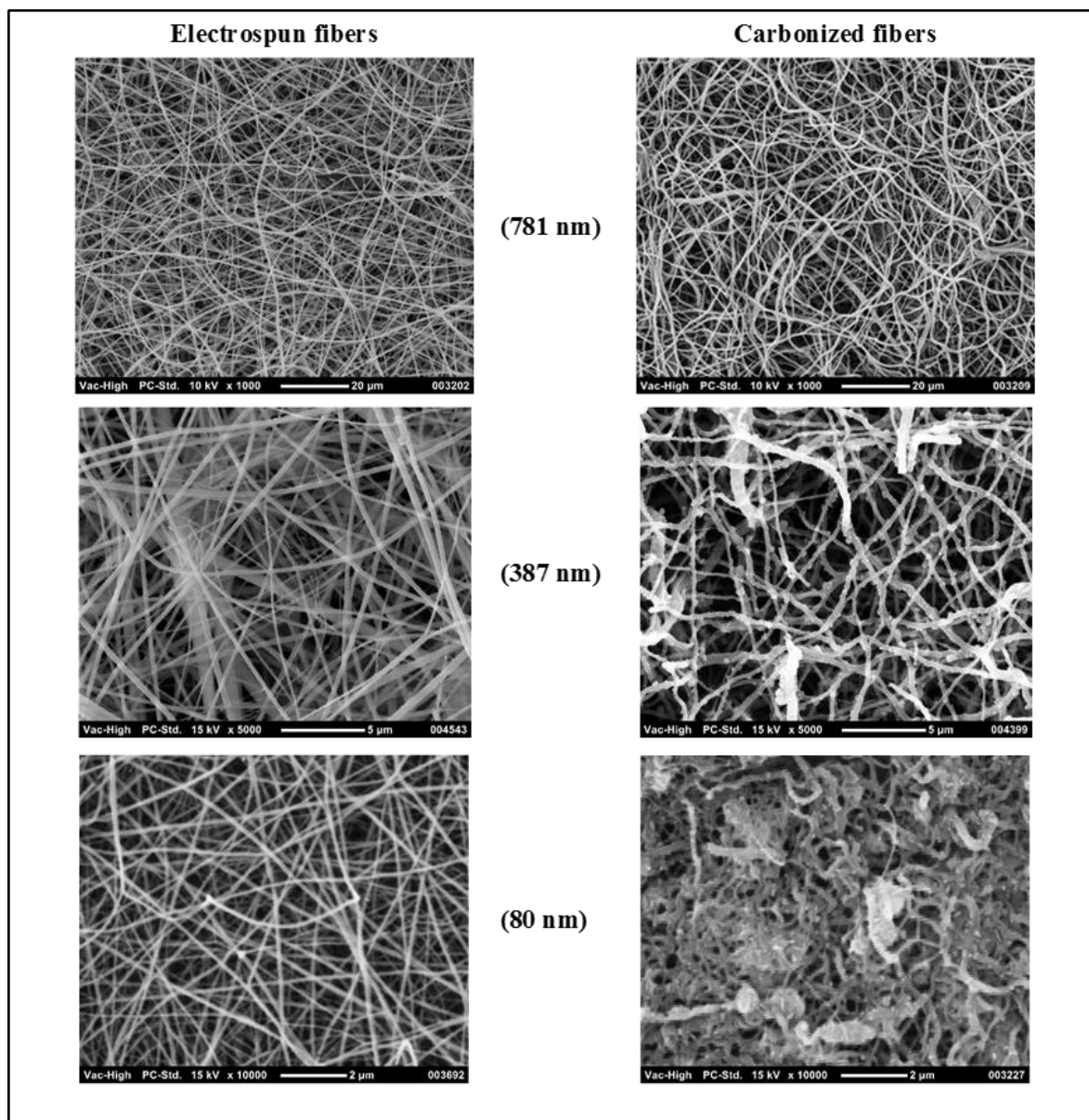


Figure 1. The carbonization outcome for the electrospun lignin/rPET fibrous mats of different average fiber diameter. The precursor mats are presented on the left, and the corresponding carbonized ones on the right.

However, precursor electrospun mats of lower average fiber diameter yield carbon nanofibrous structures in which some degree of melting is apparent. This phenomenon becomes more pronounced as the average fiber diameter is minimized; it reaches its maximum extent at the fibers of the minimum average fiber diameter of 80 nm, the thinnest nanofibers produced successfully. These precursor lignin/rPET nanofibers fuse with each other during carbonization at such a degree, that in the end the carbon morphology cannot be characterized as fibrous. Instead, there is almost complete melting, and a chunk of solid carbon is all that remains in the furnace. This phenomenon can be observed in the SEM

images of figure 1. In this figure, three representative mats of different average fiber diameter, namely 781, 387 and 80 nm, are presented. Inspection of the images reveals that the mats of 781 and of 387 nm yield a carbon fibrous morphology, while the nanofibers of 80 nm have merged with each other almost completely.

The reasons for the emergence of this phenomenon can be understood when the electrospun mats of varying average fiber diameter are examined through thermogravimetry. In figure 2, the derivative thermogravimetric curves of pure electrosprayed lignin, of pure electrospun recycled PET and of a lignin/rPET electrospun mat are shown. Pure rPET decomposes at a single stage, at around 400 °C, while pure lignin is characterized by a multi-stage decomposition, the first stage of which occurs at 200 – 250 °C. At this stage, pure lignin decomposes at a rate of 0.56 %/°C at its peak of 237 °C. The electrospun lignin/rPET mats, however, decompose with a different rate depending on their average fiber diameter. Specifically, mats consisting of relative thicker fibers (>300 nm) decompose at a stable rate of around 0.25 – 0.26 %/°C at the temperature of 237 °C. Nevertheless, this decomposition rate is much higher for the mats of minimum diameter (80 nm), for which it reaches the value of 0.40 %/°C at 237 °C. This means that in the temperature range between 200 – 250 °C, the lignin molecules existing in the thinnest fibers decompose to a much higher extent. This temperature range is crucial, as pure PET is a semi-crystalline polymer with a melting point at 250.9 °C. This means that inside the thinnest nanofibers, as much more lignin molecules decompose, the PET chains can gain some mobility; therefore, they can move more easily, and, in the end, an apparent melting behavior can be observed.

The higher decomposition rate of thinner nanofibers, although rational, has scarcely been described. Ye et al. [7] have reported that very thin (39 nm) electrospun nanofibers of PAN showed a higher weight loss during carbonization compared to thicker fibers, but their study was focused on different aspects.

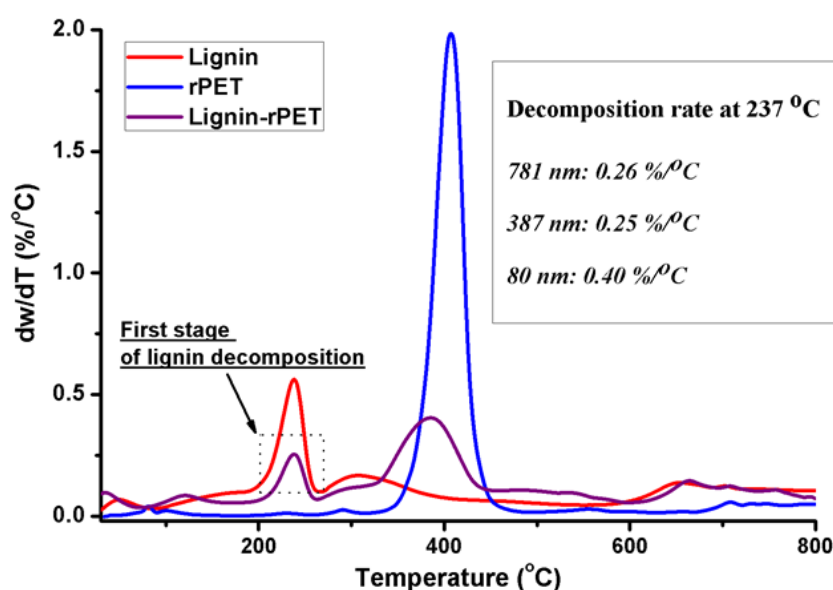


Figure 2. Derivative thermogravimetric curves of electrosprayed lignin, of electrospun rPET and of the lignin/rPET fibers.

Carbonization is a process involving the transfer of heat from the atmosphere to the surface of the fibers and then to their interior. Moreover, as the decomposition reactions take place on the surface and inside the fibers, the volatile products are transferred through diffusion from the interior of the fibers to their surface and to the atmosphere. Here, it seems that the fiber diameter is controlling the rate of these phenomena. In relatively thicker fibers, the heat and mass transfer limitations are significant and control the overall rate of the process. In contrast, in the thinnest fibers the transfer of heat and mass is faster, so these limitations are less pronounced. Therefore, here the overall decomposition rate is more

dependent on the rate of the decomposition reactions, as many more molecules are located at or near the surface of the fibers.

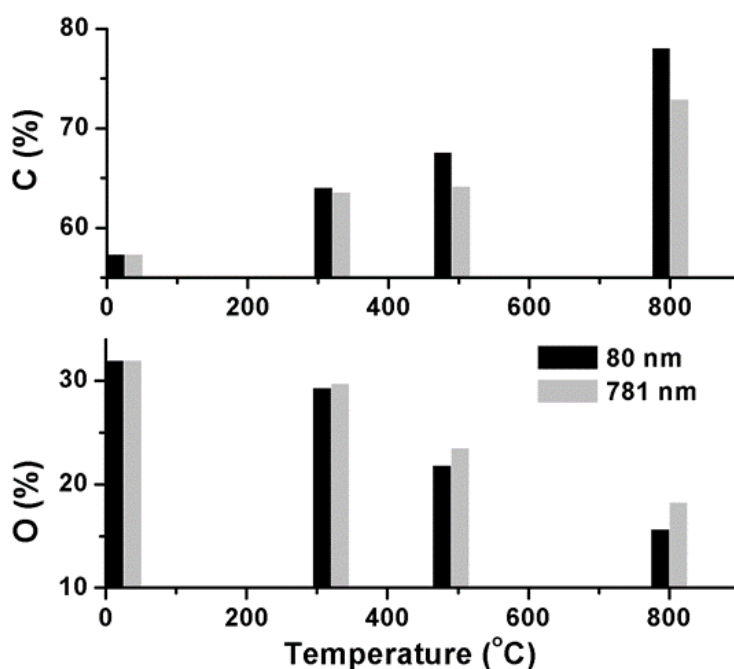


Figure 3. Carbon and oxygen content (% mass) in the fibers of 781 nm and in those of 80 nm as they are heated up to 800 °C.

As the thinnest fibers decompose at a higher rate, it is expected that during carbonization, more oxygen and hydrogen atoms will be released in the form of volatile gases, and the product will contain a higher percentage of carbon. Indeed, this assumption is confirmed through EDS, which reveals that compared to the thickest carbon fibers, the thinnest ones will contain more carbon and less oxygen (figure 3). It must also be noted, that the thinnest fibers yield a carbon material which is much stiffer and brittle than the carbon fibers produced from the thickest precursors.

4. Conclusions

In this work we have demonstrated that the nanoscale dimension controls the outcome of processes dominated by heat and mass transfer phenomena, such as the carbonization of precursor polymer fibers into carbon fibers. Although the average fiber diameter factor is usually overlooked in carbon nanofiber manufacture, here we have shown that it can determine the carbon nanofibrous morphology. In the case of precursor submicron fibers of lignin/rPET with mass ratio of 1/1, when relative thicker fibers (diameter > 300 nm) are used, carbon submicron fibers form, with average fiber diameter similar as the precursor ones. Nevertheless, when the thinnest nanofibers are used (diameter <100 nm), then there is considerable melting as the rate of lignin decomposition is maximized. To the best of our knowledge, this is the first time that the effect of the nanoscale on the carbonization process has been explicitly shown. These results underline the importance of considering the effect of the nano-dimension, when the manufacture of fine carbon nanofibers is required. Therefore, the results presented here can provide a road-map for the preparation of carbon submicron- and nanofibers not only from a blend of lignin/rPET but from other raw materials, as well.

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References

- [1] Zhang B, Kang F, Tarascon J and Kim J 2016 *Prog. Mater. Sci.* **76** 319–380
- [2] Frank E, Steudle L M, Ingildeev D, Spörl J M and Buchmeiser M R 2014 *Angew. Chemie Int. Ed.* **53** 5262–5298
- [3] Inagaki M, Yang Y and Kang F 2012 *Adv. Mater.* **24** 2547–2566
- [4] Svinterikos E and Zuburtikudis I 2016 *J. Appl. Polym. Sci.* **133** 43936
- [5] Svinterikos E and Zuburtikudis I 2017 *J. Polym. Environ.* **25** 465–478
- [6] Rodríguez Correa C, Stollovsky M, Hehr T, Rauscher Y, Rolli B and Kruse A 2017 *ACS Sustainable Chem. Eng.* **5** 8222–8233
- [7] Ye J S, Liu Z T, Lai C C, Lo C T and Lee C L 2015 *Chem. Eng. J.* **283** 304–312