PREPARATION AND CHARACTERIZATION OF CO-ELECTROSPUN LIGNIN/ALUMINA MICROFIBERS AND TUBES

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Introduction

The preparation of tubes and fibers with sizes under the micron has attracted great interest in the last years due to their promising structural, thermal and electrical properties. Electrospinning is one of the most suitable methods for preparing very thin fibrilar structures from ceramics and polymers precursors [1]. Lignin is the second most abundant polymer in nature after cellulose, being mainly obtained as a co-product of the papermaking industry. Its low cost and high availability motivated two previous works where we reported the production of carbon submicrofibers by coaxial electrospinning of Alcell lignin solutions, without any binder and achieving high specific surface areas due to a well developed microporosity [2,3]. The main drawback of this method is the necessity of a slow stabilization step in order to change the thermoplastic character of lignin to thermostable, which is required to avoid the fusing of fibers in the ongoing carbonization step [4].

Coaxial electrospinning has also been successfully used to generate polymer/inorganic composite core/sheath nanofibers. This method provides an opportunity to combine the advantages of inorganic materials, such as high chemical and thermal resistance, with the large porosity obtained when polymeric fibers are carbonized, and have been successfully used for preparing silica/PAN fibers [5]. In this work, we propose the co-electrospinning of lignin and alumina using a co-axial needle configuration. As a result, the coated fibers can be carbonized saving a great time in the stabilization step.

Experimental

Alcell ® lignin ethanol solution (1:1 weight ratio solution, ethanol CH_3CH_2OH, ≥99.5%, sigma Aldrich) and sol–gel alkoxide (Aluminum tri sec butoxide prepared with sec butyl alcohol and diethylene glycol monoethyl ether (DGME) from Sigma–Aldrich) were used as raw materials.

The lignin solution was added to the spinneret into the inner needle, while the sol-gel was poured into the outer needle. The liquids were delivered to the inner and outer needles at 4 and 0.5 mL/hour flow rates, respectively. More details about the design of the coaxial electrospinning apparatus as well as the operating conditions are given elsewhere [2,3].

The hybrid fibrous composite (lignin-alumina), noted by U, were then directly placed into an oven for an air oxidative stabilization at 200 ºC, very similar to the stabilization step that pure lignin fibers faced in previous works [2,3], but modifying the treatment times, varying from 6 to 54 hours and working directly at 200 ºC. The stabilized composites were named S06 and S24 for six and twenty four hours of stabilization time, respectively. Then the stabilized U composite, were heated at final temperatures of 600 and 900 ºC at a heating rate of 10 ºC/min in a tubular furnace, under a nitrogen atmosphere. The furnace was then let cool overnight to room temperature, obtaining composite fibers of carbon core inside an alumina shell (S06.C600, S24.C600, S06.C900 & S24.C900). On the other hand, the U composite was also directly carbonized using the same conditions previously mentioned. The resulting composites were denoted by C followed by their carbonization temperatures, C600 and C900. The S24.C900 composite was washed with hydrofluoric acid (48%, acs reagent) under continuous stirring for one hour to completely remove the alumina shell. Finally, the composites were also heated to 520 and 900 ºC under air atmosphere looking for a partial or total oxidation of the carbon core.

Results and Discussion

The micrographs compiled in Fig. 1 depict the electrospun fibers after several different treatments. On the other hand, Table 1 summarizes the surface chemistry of the samples, analyzed by means of XPS.

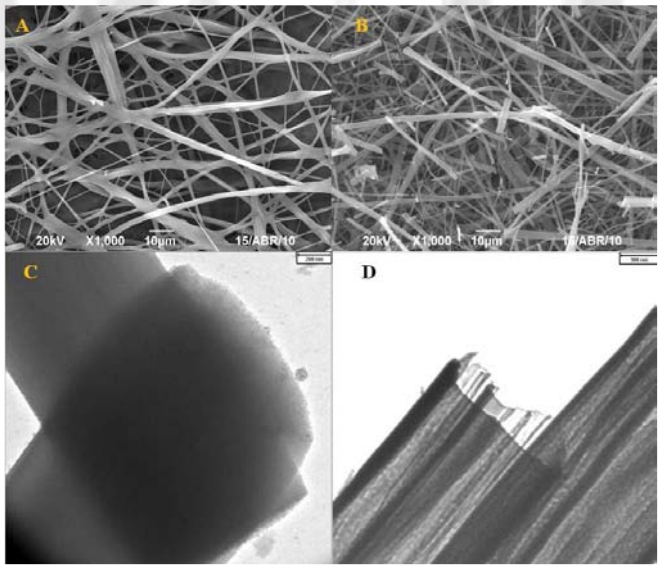

Fig. 1 SEM images of a) C900 b) S06.C900. Scale bars: 10 microns; TEM images c) S24.C900.HF and d) S24.C900.A. Scale bars: 200 & 300 nm.

The U composite proved to be long, solid fibers of rather smooth surfaces with a high distribution of sizes, ranging from

0.5 to 4 microns in diameter. XPS on Table 1 of sample U points out that alumina is located on the surface of the fiber as intended.

Table 1. Surface chemical composition of the samples.

Sample	C	O	Al	N
U	56.7	33.0	10.2	0.1
S24	54.9	36.6	8.3	0.2
C10.S24.900	68.4	22.3	8.9	0.4
C10.S24.900.HF	88.6	10.8	0.4	0.2
C10.S24.900.A	10.7	64.2	25.0	0.1

When U composite is submitted to a direct carbonization step, i.e. at 900 ºC, it still keeps a fibrous appearance, but show a high number of fused and cross-linked fibers, Fig. 1.a. This is due to lignin passing into the glassy state and leaking from the inner of the fibers during the heating treatment. The increment of carbon on the surface measured by XPS seems to support that. This problem can be solved when the composite fibers are submitted to an air oxidation treatment at moderate temperatures. The effectiveness of this treatment is supported by the increment of oxygen on S24 reported on Table 1. This oxygen is inserted between the lignin polymeric chains, strengthening the fibers [5]. Six hours at 200 ºC has been proved to be enough to thermostabilize them, avoiding the fusing of fibers, as can be seen in the image of S06.C900, Fig. 1.b. The presence of the alumina shell greatly shortens the stabilization treatment time required for solely lignin electrospun fibers [2,3]. XPS shows again an increment on the carbon content on the fiber surface, but in a lesser extent than before.

The carbonized fibers keep their shape after being treated with hydrofluoric acid. The resulting sample (S24.C900.HF) seems to be free of alumina in transmission electron microscopy images, Fig. 1.c. XPS and EDAX (not shown) also corroborates the effectiveness of the washing step. The fact that all carbon fibers keep their fibrous form after the removal of alumina confirmed that lignin constituted the continuous phase in the original as-spun fibers. On the other hand, the carbon alumina composite can be oxidized in air, giving alumina tubes as those observed in Fig. 1.d. These tubes have been prepared heating a sample of C10.S24.900 in air at 900 ºC. This treatment resulted in a global yield of 8%, very close to the 6.8% alumina content in the original fibers.

Table 2 reports the textural properties of the different samples, obtained from the N_2 adsorption isotherms at 77 K. A carbon microfiber sample (CF900) prepared by electrospinning of only lignin solutions using a method reported elsewhere [2], is also included for comparison sake. All carbonized samples show type I adsorption isotherms, characteristics of microporous materials, confirmed by the low A_t/A_{BET} ratios. The original and stabilized samples do not show appreciable N_2 uptake, while the carbonized composite at 600ºC developed a very close porosity. The low BET area measured by N_2 adsorption is confronted by a Dubinin-Raduskevich area of 510 m^2/g for CO_2 adsorption at 273 K, which allows their potential use as molecular sieves. Raising the carbonization temperature to 900 ºC improves the development of the porosity, widening the pore size and thus allowing the diffusion of nitrogen into them. When the alumina shell, which is a non porous material, of this composite is removed (C10.S24.900.HF), the BET area and micropore volume turn to be very close to those reported for CF900.

Table 2. Textural properties of the samples.

Sample	A_{BET} (m^2/g)	A_t (m^2/g)	V_t (cm^3/g)
U	3	1	0.001
S24	4	1	0.002
C10.S24.600	36	1	0.017
C10.S24.900	638	12	0.292
C10.S24.900.HF	1045	16	0.470
CF900	1195	21	0.523

Conclusions

The encapsulation of lignin inside an alumina shell allows preparation of composite electrospun fibers that can be carbonized saving a great time in the stabilization step. The presence of alumina coating the lignin does not affect to the great development of porosity that electrospun lignin fibers have previously show when carbonized at 900 ºC. The obtained carbon/alumina composites can also be properly treated to prepare alumina tubes oxidizing the carbon core or carbon fibers by washing the carbonized fibers with hydrofluoric acid. These carbon fibers are highly microporous and achieve about 1000 m^2/g of apparent surface area.

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