

PREPARATION AND CHARACTERIZATION OF LIGNIN-BASED CARBON NANOFIBER AND NANOTUBES

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Abstract

Carbon nanotubes and nanofibers have been obtained by electrospinning of a lignin based solution followed by thermostabilization at low temperature in an oxidizing atmosphere and a further carbonization step in an inert atmosphere at different temperatures, from 600 to 1000 °C. The stabilization stage increases the oxygen content of the samples avoiding the fusion of the fibers and tubes during the subsequent carbonization. The carbonization process increases the carbon and decrease the oxygen content of the samples, developing the porous structure of the fibers and tubes. Carbon nanofibers with apparent surface area of 1000 m²/g have been obtained. Both carbon fibers and tubes show a typical microporus structure with no contribution of meso- and macroporosity. SEM and TEM micrographs show carbon nanofibers and nanotubes sizes from 100 nanometers to 1 micrometer.

Introduction

Carbon nanotubes and carbon nanofibers have shown an increase potencial in a wide range of physical and chemical application, such as polymer reinforcements for composites or breakthrough materials for adsorption, energy storage, electronics and catalysis (Serp et al., 2003).

Electrohydrodynamic (EHD) forces provide a method to produce submicrometric liquid jets from a nozzle much larger in diameter than the jet itself. A liquid meniscus exiting the tip of a capillary, when subject to an appropriate electric field, deforms into a conical shape (Taylor cone), from whose tip a slender micro- or nanojet is issued. The natural fate of the jet is generally to break up into a spray of highly charged nanodroplets, fittingly known as an “electrospray” (Taylor, 1964), unless the jet solidifies before such physically natural disruption occurs. In the latter case, the EHD process has been successfully applied to produce nanofibers in a technique termed electrospinning: solidification of the liquid thread occurs while it is still in its cylindrical, metastable form (Loscertales et al., 2004).

Lignin is the major byproduct of cellulose pulp mills, where its combustion plays a critical role in the recovery process of chemical reactants remaining in black liquors after wood pulping. However, many existing paper mills become chemical recovery limited if paper production is to be maximized by increasing production rate, due to the very expensive revamping of the evaporation train needed in this case. Therefore, among other considerations of chemical and environmental concern, the development of alternative ways for lignin processing is of potential interest for pulp mills (Rodríguez-Mirasol et al., 2005).

The objective of this work is the preparation and characterization of carbon nanofibers and nanotubes from lignin by means of electro-hydro-dynamic (EHD) techniques. Lignin has a glass transition temperature far below the temperatures required for carbonization, so the fibers and tubes must be thermostabilized to prevent softening and fiber fusing. Air oxidation is a simple and low cost method of thermostabilization (Braun et al., 2005). The nanomaterials obtained have been thermostabilized at low temperatures in an oxidizing atmosphere and subsequently carbonized in inert atmosphere at high temperatures. The influence of the carbonization temperature on the porous structure and surface chemistry of the carbon nanofibers and nanotubes obtained has been analyzed.

Experimental

Nanofibers and nanotubes have been produced from electrified coaxial liquid jets generated by the injection of two immiscible or poorly miscible liquids through a pair of concentric needle to which a high electrical voltage is applied. The two liquids flow coaxially under the action of electro-hydro-dynamic (EHD) forces forming a very thin compound jet where the inner material is surrounded by a shell of the other one, producing nanotubes obtained after spontaneous or forced removal of the inner liquid or

nanofibers if both shell and core solidify coaxial. This is a method to obtain nanofibers and nanotubes in just one step. Mixtures of lignin and ethanol were electrospun to produce nanofibers that exhibited interesting mechanical characteristics. Lignin nanotubes were made from coaxial electrospinning of the lignin based solution (shell) and a regular liquid (core).

The lignin nanotubes and nanofibers were thermostabilized by heating from room temperature to 250 °C at a heating rate of 0.05 and 0.10 °C/min, respectively, in a tubular furnace under an oxidizing atmosphere (150 cm³ STP/min of air). The stabilized fibers were subsequently carbonized in the same tubular furnace with a flow of 150 cm³ STP/min of N₂ at different temperatures, from 600 to 1000 °C,. The heating rate in the carbonization stage was 10 °C/min. The stabilized nanotubes were carbonized at 1000 °C at the same conditions as the stabilized fibers. Carbon fibers and tubes were denoted by CF or CT, respectively, followed by the carbonization temperature in Celsius degrees.

The ultimate analysis of the carbon nanofibers and nanotubes were performed in a Leco CHNS-932 system, being the oxygen content calculated by difference. The porous structure was characterized by N₂ adsorption-desorption at -196 °C and by CO₂ adsorption at 0 °C, carried out in an Autosorb-1 model of Quantachrome. Samples were previously outgassed during 8 hours at 150 °C and at 50 mtorr. From the N₂ adsorption/desorption isotherm, the apparent surface area ($A_{\text{BET}}^{\text{N}_2}$), the micropore volume ($V_{\text{t}}^{\text{N}_2}$) and the external surface area ($A_{\text{t}}^{\text{N}_2}$) were calculated. The narrow micropore surface area ($A_{\text{DR}}^{\text{CO}_2}$) and micropore volume ($V_{\text{DR}}^{\text{CO}_2}$) were obtained from the CO₂ adsorption isotherm.

The surface chemistry of the samples was studied by X-ray photoelectron spectroscopy (XPS) analysis. XPS analyses of the carbons were obtained using a 5700C model Physical Electronics apparatus with MgK α radiation (1253.6 eV). The surface morphology was studied by scanning electron microscopy (SEM) using a JSM 840 JEOL microscope working at 25 KV voltage and by transmission electron microscopy (TEM) in a Philips CM200 microscope at an accelerating voltage of 200 kV.

Results and Discussions

Table 1 reports the ultimate analysis of the Alcell lignin, the fibers obtained from this lignin and CT-1000 carbon nanotube. The stabilization process increases the oxygen content of the fiber. This stage increases the glass transition temperatures of the fibers avoiding the fusion during the subsequent carbonization process (Braun et al., 2005). Carbonization of the stabilized lignin nanofibers produces an increase in the carbon content. The increase in the carbonization temperature produces fibers with higher carbon and lower oxygen contents. The ultimate analysis of CF-1000 and CT-1000 reveal no significant differences between fibers and tubes. Similar conclusions were obtained from the XPS analysis.

Table 1. Ultimate analysis for Alcell Lignin, lignin-based fibers, stabilized fibers and carbonized fibers at different temperature.

	%C	%O	%H	%N
Alcell Lignin	66.20	27.42	6.18	0.18
Non Stabilized Fibers	68.74	24.67	6.31	0.20
Stabilized Fibers	62.15	33.68	3.80	0.37
CF-600	82.66	13.92	2.99	0.43
CF-800	85.28	12.86	1.38	0.48
CF-900	90.29	7.89	1.32	0.50
CF-1000	93.78	4.41	1.26	0.56
CT-1000	92.27	4.89	2.38	0.46

Both non stabilized and stabilized fibers show very low N₂ adsorption, with apparent surface areas lower than 1 m²/g. Figure 1 shows the N₂ adsorption-desorption isotherms for CF-800, CF-900 and CF-1000 carbon nanofibers and CT-1000 carbon nanotube. The isotherms are type I according to IUPAC classification, typical of microporous structures. The increase of the carbonization temperature up to 900 °C produces fibers with a more developed microporous structure. However, a further increase in the carbonization temperature seems to produce shrinkage of the microporous structure. The porous structure of the carbon nanofiber and nanotube obtained at the same carbonization temperature (CF-1000 and CT-1000) is very similar, as revealed by the comparable N₂ isotherms. Table 2 summarizes the porous structural parameters for the different carbon nanofibers and the carbon nanotube obtained. Carbon nanofiber CF-900 presents an apparent surface area higher than 1200 m²/g. All carbon nanofibers and carbon nanotubes show a very high narrow micropore surface area ($A_{\text{DR}}^{\text{CO}_2}$) and volume ($V_{\text{DR}}^{\text{CO}_2}$) due to

the presence of a developed narrow microporosity and low external area values ($A_t^{N_2}$) characteristics of a poor developed mesoporous structures.

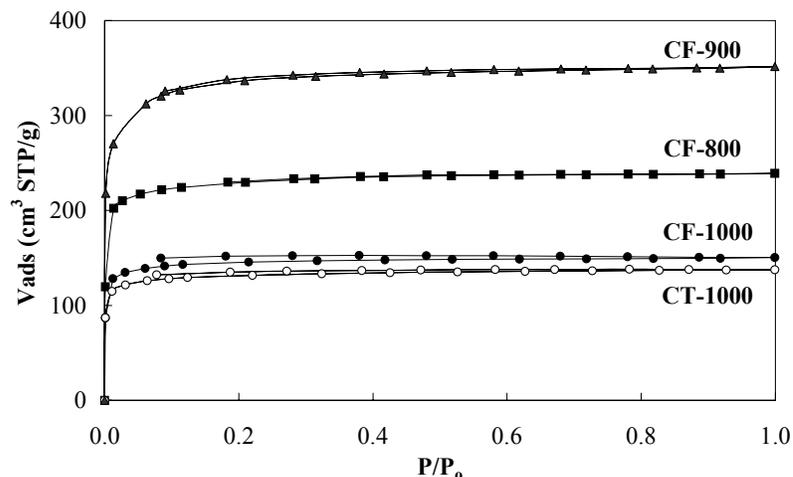


Figure 1. N_2 adsorption-desorption isotherms at $-196\text{ }^\circ\text{C}$ for CF-800, CF-900 and CF-1000 carbon nanofibers and CT-1000 carbon nanotube.

Table 2. Porous structural parameters of lignin-based carbon nanofibers and nanotubes.

	$A_{BET}^{N_2}$ (m^2/g)	$V_t^{N_2}$ (cm^3/g)	$A_t^{N_2}$ (m^2/g)	$A_{DR}^{CO_2}$ (m^2/g)	$V_{DR}^{CO_2}$ (cm^3/g)
CF-600	772	0.330	6	884	0.337
CF-800	842	0.361	8	946	0.360
CF-900	1249	0.523	17	910	0.347
CF-1000	534	0.228	3	934	0.356
CT-1000	477	0.204	8	681	0.259

Figure 2 a and b present SEM micrographs for non stabilized lignin fiber and CF-1000 carbon nanofibers. Non stabilized fibers show higher size than the fibers obtained after carbonization at $1000\text{ }^\circ\text{C}$. As carbonization temperature is increased a reduction in the fiber size is observed.

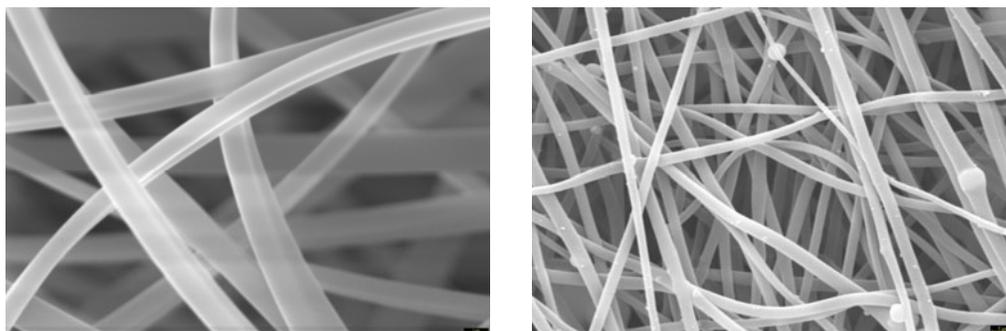


Figure 2. SEM micrographs for (a) non stabilized fiber and (b) CF-1000 (bar length: $1\text{ }\mu\text{m}$).

Figure 3 depicts two TEM micrographs for (a) carbon nanofiber CF-1000 and (b) carbon nanotube CT-1000. Both fibers have a size of around $300\text{-}400\text{ nm}$. In the case of the carbon nanotube, the thick of the walls of the tubes is of around $75\text{-}100\text{ nm}$, with the internal diameter of around 150 nm .

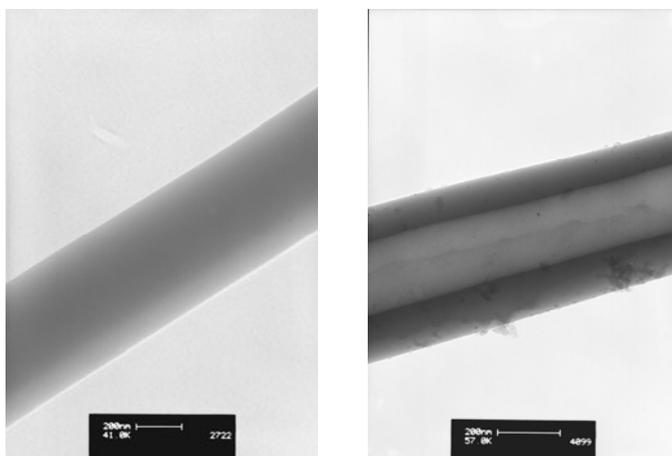


Figure 3. TEM micrographs of (a) CF-1000 carbon nanofiber and (b) CT-1000 carbon nanotube (bar length: 200 nm).

Conclusions

Carbon nanotubes and nanofibers have been obtained by electrospinning of a lignin based solution. Prior to carbonization a stabilization stage is required in order to avoid the fiber fuse during carbonization. This last process increases the carbon content and develops a very microporous structure. As carbonization temperature increases a decrease of the fiber size is observed. The size of carbon nanofiber and nanotubes obtained is from 100 nanometers to 1 micrometer.

References

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