

Synthesis of Carbon Nanostructures from Residual Solids Waste Tires

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ABSTRACT: This article presents the results of the synthesis and morphological characterization of carbon nanostructures obtained from the decomposition of residual solid from waste tires (RSWT) in quartz tubes under reduced pressure (1.33 Pa) at 900°C for 15 min. The synthesis led to the formation of two phases, a fragmented solid black powder composed of multi-walled carbon nanotubes (MWCNTs), onion-type fullerenes, and spheres, and a very bright metallic dark film. Analysis by microscopy (SEM and TEM) showed that the MWCNTs had an average diameter of approximately 25 nm and a length greater than 100 nm while the diameter of the onion-type fullerenes was found to be 8 nm. The nanospheres showed

different diameters ranging from 500 nm to 1.5 μm , and some had a metallic core surrounded by layers of carbon. The infrared spectra of the nanotubes exhibited absorption bands at 1558 and 1458 cm^{-1} , corresponding to C=C and C—C bonds, and signals at 3438 and 1080 cm^{-1} related to the OH and C—O groups from oxidized graphite as it was identified in the dark film. The Raman spectra of the carbon nanostructures present D and G-bands at 1331 and 1597 cm^{-1} , respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1960–1967, 2012

Key words: multi-walled carbon nanotubes; MWCNTs; onion; residual solids waste tire; nanospheres

INTRODUCTION

Because of the massive worldwide production of tires and the technical difficulty of recycling them at the end of their functional life, discarded tires have become one of the most serious environmental problems in recent years. Recycling tires can be very difficult due to the thermosetting nature of the cross-link molecular structure. Several methods for recycling tires have been developed such as nitric acid digestion, electric and calorific energy conversion, and pyrolysis in a vacuum or inert atmosphere.¹ The main purpose is to recover some carbon compounds and to destroy any hazardous components within the tires. Tire pyrolysis has proven to be a good method for the recovery of carbon in solids up to 93% by weight at 450°C.^{2,3} In previous work, a solid powder that was obtained from car tires by pyrolysis and thermal shock was fully characterized. It was

demonstrated that a powder that was rich in carbon compounds could easily be obtained.⁴ This carbon residue can be used as the main precursor during the synthesis of carbon nanostructures (i.e., carbon nanotubes (CNT), fullerenes, nanospheres, and graphite film). Murr et al., injected ground tire as the secondary carbon source during the synthesis of CNT using electric arc-discharge.⁵

Nanostructures of carbon, such as CNT, fullerenes, onions, films, and nanospheres, have attracted great academic and technological interest due to their excellent physical, mechanical, and electronics properties.⁶ These materials have been extensively studied for several applications, such as electronic and thermal devices, gas storage systems (H_2 and CO_2), and catalytic supports, among others.⁶ Carbon nanostructures are synthesized by the diffusion of carbon through a metal catalyst and its subsequent precipitation and growth as graphite filaments. In the past decade, many preparation methods for carbon nanostructures have been developed, such as electric arc discharge, laser vaporization, hydrocarbon pyrolysis, flame synthesis, and chemical vapor deposition (CVD), which are the three most widely used techniques. Among these three techniques, CVD is most commonly employed because of the relatively low cost of the equipment required. In

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addition, CVD can be easily managed to obtain large quantities of carbon nanostructures, generally of CNTs.⁷

Several nanostructures have been obtained from different carbon source. Equally important, elevated purity carbon sources are often needed for their synthesis. Hydrocarbon vapors have been the dominant choice as a carbon source, mainly because of the preference for the synthesis of these compounds using CVD. Graphite, carbon containing gases (methane, acetylene, propane, and carbon dioxide), and related organics in the liquid form (benzene, toluene, and methanol) are the most common source of carbon to synthesize carbon nanostructures.^{6–8} However, recent investigations have carried out the synthesis using polymers (polyethylene, polypropylene, polymethyl-methacrylate, and polytetrafluoroethene) as primary carbon sources, especially using the CVD and electric arc discharge synthesis methods.^{7,9–13}

The information on the carbon sources for the solid-state synthesis of carbon nanostructures is still very limited, but numerous studies have indicated the crucial role played by a metal in CNT, onion, and fullerene synthesis. Metals that have shown the greatest promise in this regard are Fe, Co, and Ni.^{6,8}

Many parameters, such as pressure, reaction temperature, gas composition and flow rate, reaction time, catalyst natures and sizes, have been reported to affect the nature of the carbon species in the resulting material. However, the effect of the above parameters for the growth mechanism of carbon nanostructures is still unclear. The present work focuses on the synthesis and chemical and morphological characterization of different carbon nanostructures obtained by chemical reaction in quartz tubes employing powder acquired from waste car tires by a thermal shock process⁴ as the primary carbon source and with ferrocene as the catalyst. The main objective of this work is the utilization of residual solid from waste tire (RSWT) as a new alternative carbon source for the synthesis of carbon nanostructure by simple deposition technique in a quartz tube reactor, also to provide a method of reducing the waste and pollution generated by discarded tires.

EXPERIMENTAL

Materials

The side wall of a Bridgestone Firestone Tire was used to obtain the carbon source. The catalyst was ferrocene (reagent grade 98%, ζ -Aldrich, Sigma-Aldrich Chemical Company, Toluca, México), liquid and gaseous nitrogen (99 +%), tetrahydrofuran (reagent grade 99%, ζ -Aldrich), and quartz tubes (14 ID

\times 19 OD \times 320 mm L) supplied by Quartz Scientific, Inc. (Fairport Harbor, OH, USA) were also used.

Obtaining the carbon source

The method for obtaining the carbon source consisted of pulverizing the tire and then applying a thermal shock to small pieces of the sidewall of the tire that were placed in a crucible and heated in a furnace to 400°C for 10 min in a nitrogen atmosphere with a flow of 3 L/min. Immediately afterwards, the samples were immersed into liquid nitrogen until the nitrogen was evaporated. The residues were manually pulverized in an agate mortar to obtain a fine powder that will be referred as the RSWT. Physical and chemical characterization of the RSWT has been reported in previous work.⁴ However, the molecular weight of the polymeric residue in the RSWT and the thermal degradation process were obtained by gel permeation chromatography (GPC) and thermo gravimetric analysis (TGA), respectively. The GPC equipment was a Hewlett-Packard model Agilent 1100 system, equipped with a Zorbax 1000S column and a refractive index detector. The elution was performed with tetrahydrofuran (THF) at 1 mL/min and 25°C. The TGA was carried out using a Perkin-Elmer Thermal Analyzer model TGA 7 in a temperature range of 25–750°C to a heating rate of 10°C/min with samples of RSWT of 7 mg under N₂ atmosphere.

Synthesis of carbon nanostructures

The synthesis of the carbon nanostructures was carried out by mixing 100 mg of RSWT along with 6 mg of ferrocene (FeCp₂). Subsequently, the mixture was added to the quartz tube, which was evacuated (up to 1.33 Pa) for 1 h and sealed. In agreement with previous studies on obtaining nanostructures as a function of temperature and time, the heating process began at 25°C, and the temperature increased at rate of 30°C/min up to 900°C, where it remained for 15 min, and was later cooled to 25°C. Finally, the tubes were opened, and the residual solid material was collected and analyzed.

Characterization of the carbon nanostructures

The material obtained from the synthesis was coated with gold in a Denton Vacuum-Desk II sputtering system and was analyzed morphologically and elementally with a scanning electron microscope (SEM) Phillips XL30 fitted with an energy dispersive X-ray system (EDS) operated under high vacuum in the 20–25 keV range. The residues were also analyzed by transmission electron microscopy in a JEOL JEM-

2010F High Resolution Transmission Electron Microscope (HRTEM) operated at 200 keV with a point to point resolution of 1.9 Å. Prior to the TEM analysis, the samples were grounded in an agate mortar, suspended in isopropyl alcohol and placed in an ultrasonic bath for 2 min to disperse the particles. A drop of the suspension was placed on a copper grid of 300 meshes and coated with Formvar and amorphous carbon. The interplanar distance measurements were performed using the software Digital Micrograph Version 3.7.0. The synthesized multi-walled carbon nanotubes (MWCNTs) were compared with commercially available nanotubes (Baytubes®C150P; Bayer Material Science, Leverkusen, Germany; www.baytubes.com) by SEM analysis.

Characterization by Fourier Transforms infrared spectroscopy was carried out on KBr-disks containing small quantities of the synthesized material. The analysis was performed on a Thermo Nicolet Spectrometer (Nexus 670, FTIR), and the data acquisition parameters were 64 scans with a resolution of 4 cm⁻¹ and range of 400–4000 cm⁻¹. The Raman spectra were performed at room temperature, on micro Raman spectrometer (Kaiser optical system, 50× objective lens and Andor DV401 CCD camera) with He-Ne laser at an excitation wavelength of 632.8 nm (1.96 eV) and powder of 35 mW in a range of Raman shifts from 800 to 1800 cm⁻¹ in the synthesized products and RSWT.

RESULTS AND DISCUSSION

Chemical composition of the residual solids waste tire

The RSWT obtained was principally composed of a polymeric fraction (extractable with THF), amorphous carbon, zinc oxide (ZnO), and calcium carbonate (CaCO₃) as the main compounds.⁴ During preparation (and in the relatively short heating time), —S—S— and C—S bonds in the polymeric fraction were broken, mainly because their binding energies (317 and 276 kJ mol⁻¹, respectively) were lower than those of the C—C and C=C bonds (334 and 606 kJ mol⁻¹).¹⁴ Therefore, the polymeric chain underwent a rearrangement during the heating time, yielding polymers of a low molecular weight of approximately 14,000 g mol⁻¹ and a polydispersity of 1.06, which corresponds to polystyrene. The chemical composition of RSWT was very similar to the residual solid reported in the literature,^{2,15} although each tire manufacturer has a different formulation.¹⁵

The thermal degradation of the RSWT began approximately at 310°C and presented a maximum degradation at 515°C, as shown in Figure 1. The initial degradation, between 310 and 450°C, corresponds to the polymeric phase (polystyrene)

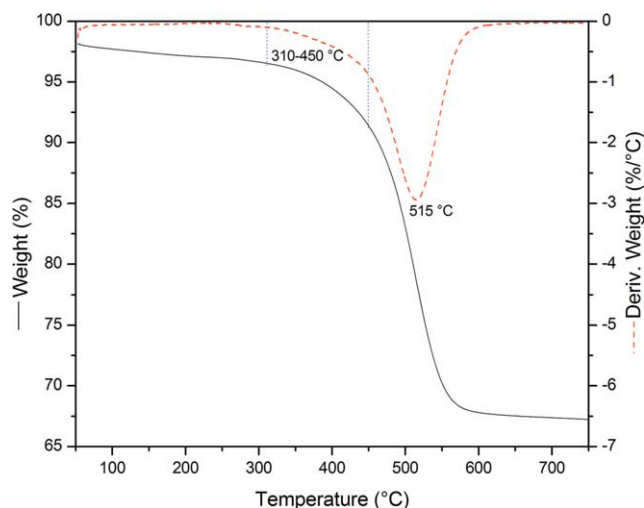


Figure 1 Thermogram of RSWT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

remaining in the RSWT, whereas the carbonaceous residues (carbon black, amorphous carbon, and others) are degraded at 515°C.^{16–19} The complete degradation of RSWT was carried out to temperatures above 750°C in oxygen or air due to the residual carbon black in the RSWT.²⁰ Thus 900°C was the minimum temperature to obtain carbon nanostructures in this work. It should be noted that carbon black has been used as a carbon source to obtain double wall CNT.²¹

Obtaining carbon nanostructures

Most of the processes for obtaining carbon nanostructures (using the techniques explained in the literature)⁷ make use of carbon sources and high purity gases as carriers to increase the yield of the final material. The main contribution from this work is the simple and economic methodology used to acquire nanostructure particles utilizing the RSWT as the primary carbon source and substituting the carrier gas with a vacuum (up to 1.33 Pa) during the nanostructure preparation. The time and the temperature to obtain nanostructures from RSWT are reported here; these parameters can be varied to select the nanostructures of interest. It should be noted that, in this article, the potential of RSWT to be used as a new carbon source for the synthesis of nanostructures is reported. The quartz tube after the synthesis presented the formation of two phases, principally a fragmented solid black powder and a very bright metallic dark film.

Figure 2 presents the scheme of the heating process to obtain the nanostructures. Several steps are presented with increasing temperature, which are described based on the research reported and the data obtained from RSWT in the TGA (Fig. 1). It is

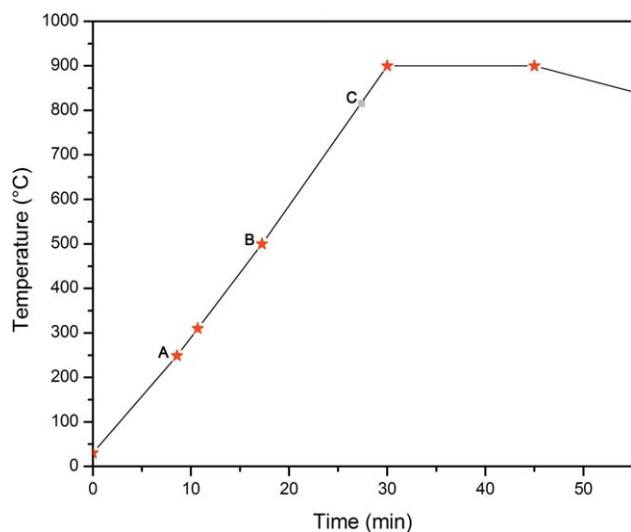


Figure 2 Scheme of the heating process used to obtain carbon nanostructures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suggested that at 249°C, the FeCp_2 contained in the mixture vaporizes (point A) and, with increasing temperature, waste polymers contained in the RSWT are degraded (between 310 and 450°C). Above 500°C (point B), C–H and Fe–C bonds of FeCp_2 are broken to form Fe metallic particles,²² dimers and trimers, and maximum degradation occurs for the carbonaceous residues from the RSWT that are deposited on the surface of Fe particles for growth of nanotubes (point C). The metal particle size and the excess carbon deposited on the particles favor nanospheres formation.^{23,24} The film formation may start

at low temperatures (between 600 and 750°C) due to the saturation of the carbon atoms during the degradation of the RSWT.

Scanning electron microscopy

SEM analysis confirmed the formation of nanospheres in the powder, whose diameters varied from 500 nm to one μm [see Fig. 3(a–c)], sheets [Fig. 3(b,d)] and agglomerates formed by some spheres that apparently collapsed during the heating [Fig. 3(c)]. Moreover, in some areas, the presence of fibrous structures was detected inside the circles [Fig. 3(d,e)], similar to that seen in Figure 3(f).

Elemental analysis by EDS

Table I presents the elemental composition (atomic percentage) obtained during analysis by EDS at the point and area of the nanostructures (spheres, sheets, and clusters), which revealed that they consisted mainly of C, Fe, O, S, and Zn. Sulfur and zinc were expected to be present because the RSWT contained zinc oxide and zinc sulfide. However, the sulfur was also a component of the polymer fraction obtained during the thermal shock process of the RSWT. Silver (Ag) and gold (Au) from the sample holder and coating of the sample are likewise detected by EDS. Analysis of the sheets showed a relatively high concentration of Ag and Au, mainly because the structures had a thickness of about 100 nm to 200 nm, and thus the electron beam penetrated the sample holder and supporting tape.

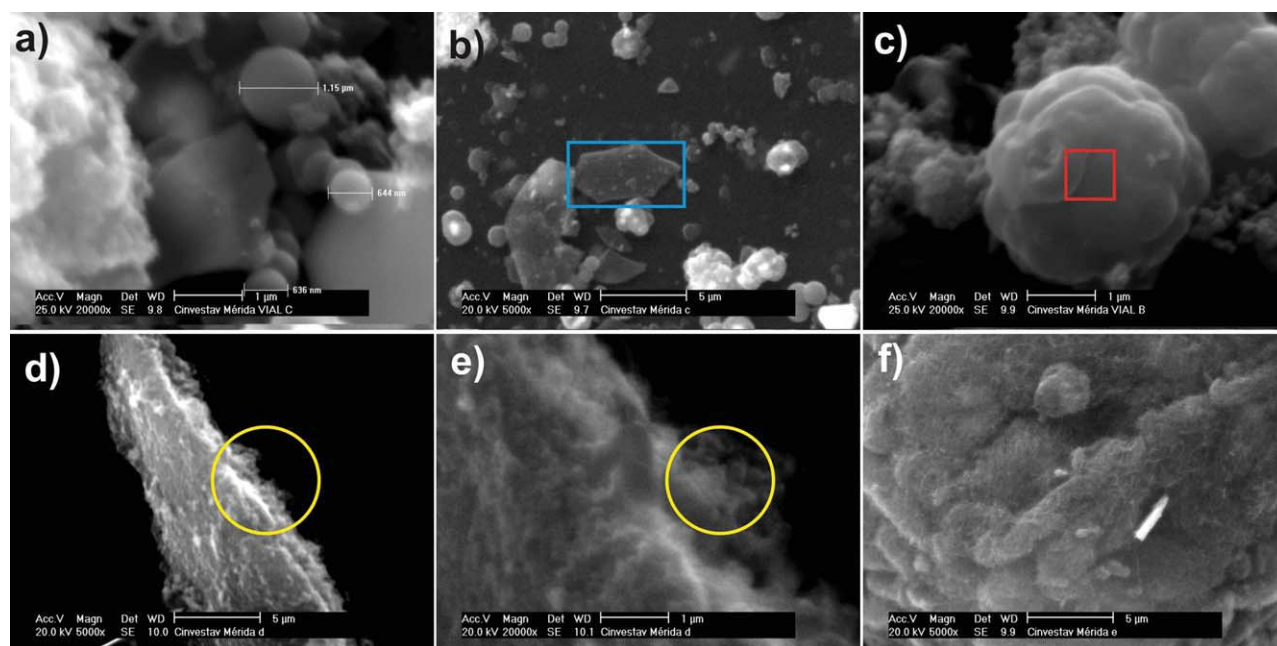


Figure 3 SEM micrograph of the material obtained at 900°C (a–e) and commercial multi-walled carbon nanotubes (Baytubes®C150P) (f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Chemical Composition of Representative Nanostructures
by EDS (atomic %)

Element	Materials		
	Spheres	Sheet	Cluster
C	86.28	83.46	94.06
Fe	0.2	0.57	1.58
O	6.64	6.06	3.29
S	–	–	0.19
Ca	–	–	0.20
Zn	–	–	0.03
Au	0.53	0.41	0.23
Ag	6.35	9.16	0.42
Si	–	0.34	–

–: not detected.

The iron identified in the spheres may be indicative of the formation of metallic core-shell spheres because the punctual analysis of the core showed a higher concentration of Fe in comparison with the direct analysis of its periphery, which was verified by carrying out the punctual EDS analysis in the center (r_0), at half the radius ($r/2$) and in the periphery (r) of several spheres that were randomly selected. The results are exhibited in the Figure 4.

Additionally, the development of spheres and CNT was intimately related to the quantities of metal particles (Fe) present in the reaction. As the number of metal particles increased, the formation of spheres was enhanced, which was observed by varying the concentration of the catalyst during the synthesis process. It was also observed by He et al.²⁵

Transmission electron microscopy

The measurement of lattice-fringe spacing and angles recorded in digital high-resolution electron micrographs was made using computer analysis of reciprocal space parameters (FFT), according to the Ruijter et al. method.²⁶ With this method it is possible to estimate an error of 0.01 nm, even lower. Figure 5 shows HRTEM images of as obtained onion-type fullerenes [Fig. 5(a,d,e,f)] and MWCNTs [Fig. 5(a–d)], whose diameters were about 25 nm and lengths were greater than 100 nm, with an inner diameter of roughly the interplanar distance of planes of graphite, $d_{111} = 0.336$ nm. Similar interplanar distances are presented in Figure 5(f), corresponding to an onion-type fullerene structure with a diameter of about 8 nm. These structures are very similar to those reported in the literature.²⁷ However, the primary carbon sources employed in the previous investigation were benzene, acetylene, and ethylene, and the diameters of the nanostructures found ranged from 2 to 30 nm. This comparison demonstrates that the RSWT can be used as the car-

bon source to obtain nanospheres, providing a simple and economical alternative for the synthesis of these structures.

The synthesis of carbon nanostructures from RSWT involves the degradation of polymeric residue, carbon, and gases generated during the heating process such as methane, ethane, propane, butane, CO, and CO₂. These gases are also produced in the pyrolysis of tires at 400°C in the absence of oxygen. Other compounds that are generated include CS₂ and SH₂,^{28,29} aromatic compounds, and aliphatic C₅–C₂₀, carbon black, ZnO, ZnS, and CaCO₃.⁴ However, not all these compounds can be utilized to synthesize carbon nanostructures because each compound has a different degradation mechanism, which leads to the formation of defects and increases the contaminants in the nanostructure. In general methane, ethylene, propane, butane, CO, and CO₂ are used to synthesize less contaminated carbon nanostructures.^{8,30}

The advantage of using the thermal shock method is that the RSWT obtained can be purified to remove inorganic compounds such as ZnO, ZnS, and CaCO₃ with hydrochloric acid to produce the polymeric residue with carbon-free of these impurities, which facilitates their decomposition to gases such as methane, ethane, propane, CO, and CO₂. This methodology can yield a higher number of RSWT.

The formation of nanospheres in the reaction occurring within the vacuum quartz tube can be compared with those obtained by Chen et al., who used polypropylene as the carbon source and ferrocene as a catalyst.⁷ Similarly, Chen et al., obtained CNT from carbon black.²⁴ Consequently, the appearance of carbon spheres during the nanostructure

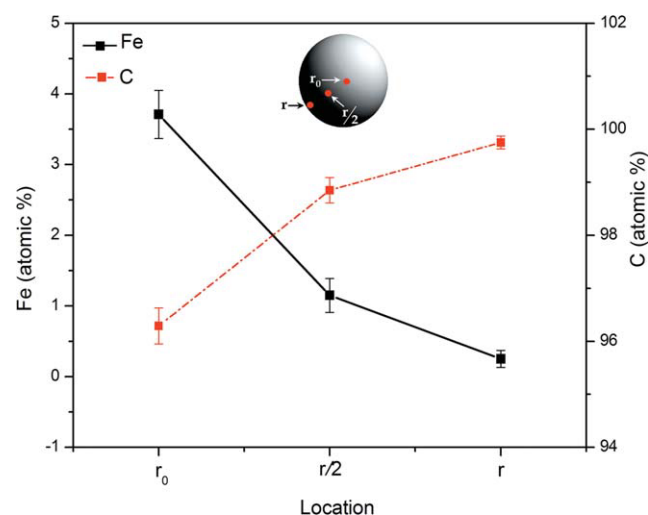


Figure 4 EDS analysis: percentage atomic of Fe and C as a function of the analysis location. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

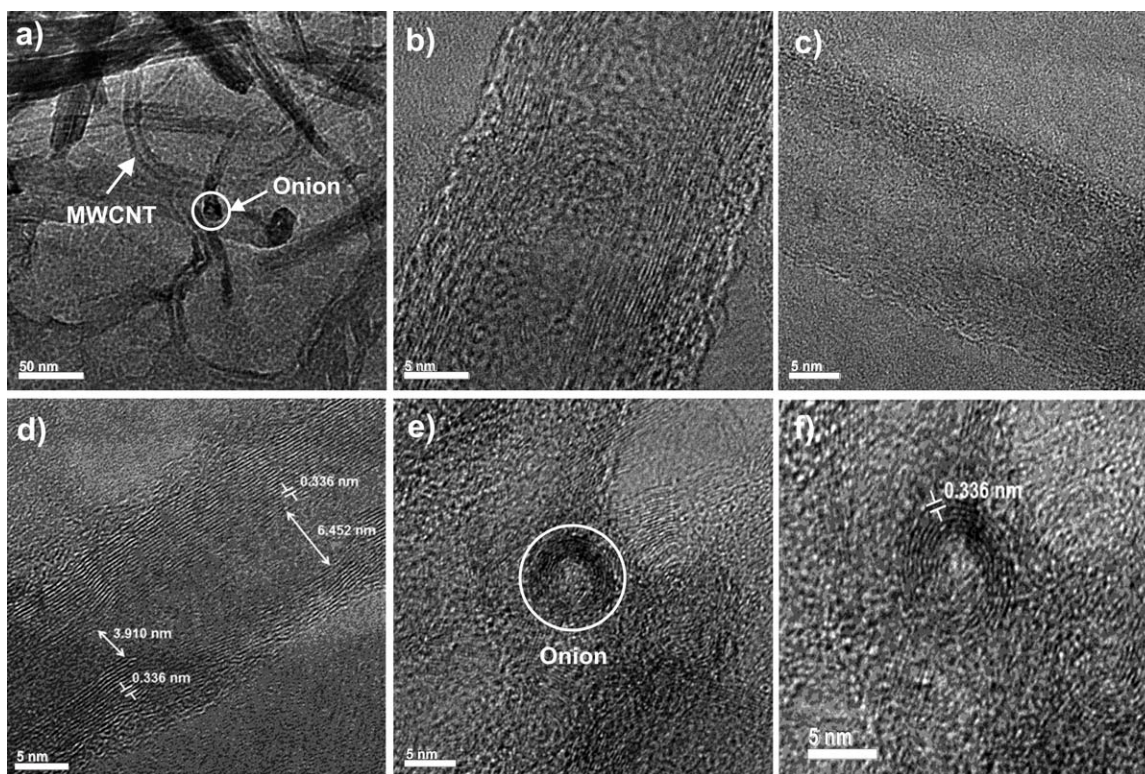


Figure 5 HRTEM micrograph of the material obtained: multi-walled carbon nanotubes (a–d) and onion-type fullerenes (e,f).

synthesis seemed to result from both the presence of polymer residues and the presence of remaining carbon black in the RSWT (used as the primary carbon source).

On the other hand, although the presence of sulfur in the nanostructures is indicative of the partial degradation of the tire, it cannot be considered a contaminant, because the literature reports the use of this element (S) for obtaining different carbon nanostructures,³¹ MWCNTs and double wall nanotubes,^{32–34} and it is very probable that the presence of sulfur in RSWT contributes to the formation of these types of carbon nanostructures.

Infrared Spectroscopy

The analysis by FTIR of the film, powder, and mixture obtained during the synthesis is shown in Figure 6. The infrared spectrum exhibits absorption bands at 2922 and 2852 cm^{-1} that are assigned to C=C–H asymmetric and symmetrical stretching bonds. Small peaks around 1558 cm^{-1} can be assigned to carbon vibration of the aromatic ring (the stretching of the conjugate bonds of C=C), whereas the absorption at 1458 cm^{-1} is related to the C–H groups. The IR peaks at 3438, 1630, and 1080 cm^{-1} are associated with the C–O vibrations from the adsorption of H_2O molecules of the KBr or graphitic nature (C=C) of the carbon.^{35–38}

For most carbon nanostructures, the carbon skeleton stretching vibrations can be found at 1558 cm^{-1} .^{38–41} The signals of the C=C bonds are present in the three samples. However, they are more defined and have a greater intensity in the spectrum of the powder due to the presence of CNTs. Because of the history of carbon nanostructures, it is possible

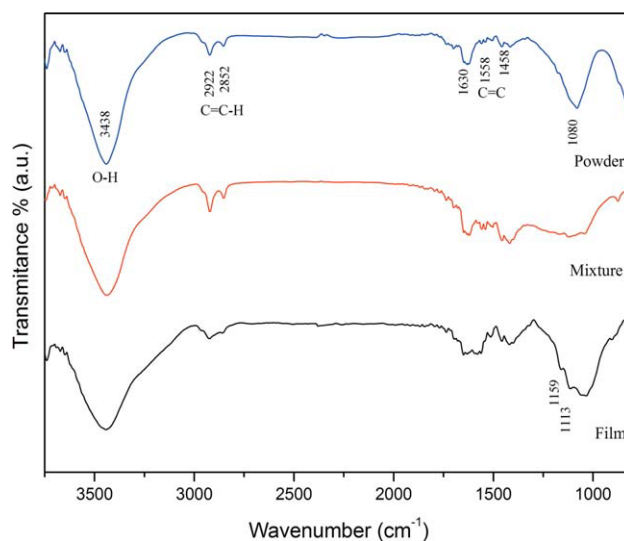


Figure 6 Infrared spectrum of the synthesized material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

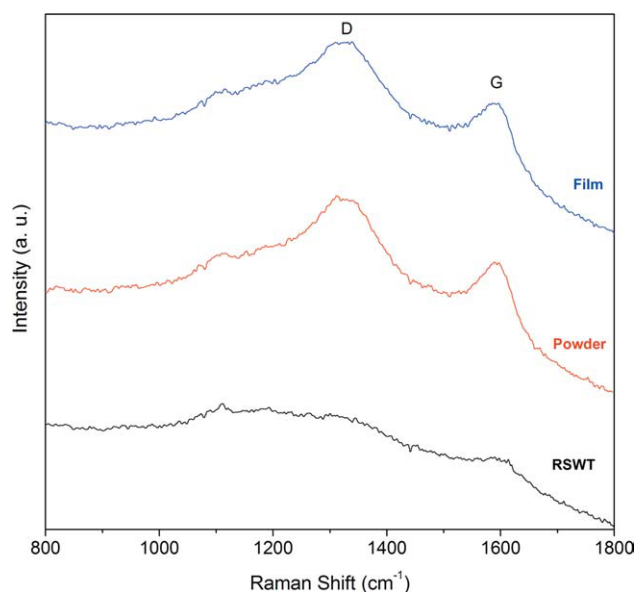


Figure 7 Raman spectrum as synthesized materials (film and powder) and RSWT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that some heteroatoms, such as oxygen, can be incorporated in the structure during synthesis. The C=C band conjugated with adjacent C=O results in the IR absorption of this band varying more strongly or weakly. A characteristic band that is correlated with defects or disorder in the nanostructures is found at 1458 cm^{-1} .³⁸ The powder phase was not subjected to a previous purification process, and thus vibrational signals regarding functional groups, such as C—O, C—H, can be identified. At this stage, the ability to use RSWT for obtaining carbon nanostructures can be evaluated. On the other hand, the film phase presented signals at 1113 and 1159 cm^{-1} , attributed to C—C and C—O bonds, possibly because the film was composed of a graphitic carbon in the oxidized state.

Raman microscopy

Raman microscopy is a fast and nondestructive tool to evaluate the crystallinity and defects in carbon structures. Figure 7 shows the Raman spectra of RSWT and the synthesized products, film, and powder. The spectrum confirmed the existence of crystalline and amorphous structures in both the film and the powder, to present two strong bands at 1593 and 1336 , 1597 and 1331 cm^{-1} , respectively. These results are similar to the reports in the Refs. 9–12, 31, 41, 42; however, in these references the authors used high purity of carbon sources such as methane, xylene, polypropylene, polyethylene among others, while in this work, the carbon source used to synthesize of carbon nanostructures was a solid residue (RSWT) obtained from waste tires. As well as being used as a new car-

bon source, the RSWT could reduce the pollution they generate by solid residuals of waste tires.

The band called G is related with the E_{2g} mode of hexagonal graphite and is attributed at stretching vibration of sp^2 hybridized carbon atoms in a graphite layer, while D-band corresponded to the A_{1g} in-plane breathing vibration mode caused by defects in the plane of graphite.^{9–12,31,41,42} On the other hand, the intensity ratio between of D-band and G-band (I_D/I_G) are usually used to characterize the graphitization degree of carbon materials.^{9–12,31,41,42} Thereby, to obtained value for the film and powder of 0.75 and 1.2, respectively, indicated that film present fewer defects than powder. This difference is attributed not to carry out the purification process in the powder. Further microscopic analysis after the removal of the amorphous fraction would be conducted and reported in the future. The impurities were watched equally in the FTIR analysis, to present band of methyl and methylene and functional groups such as C—O and —OH in the film and powder. The RSWT showed a small G-band due to carbon black used in tire manufacturing.^{4,20}

CONCLUSIONS

A novel technique, based on CVD, was developed for the synthesis of carbon nanostructures from the new carbon source that is the residual solids of waste tires. Analysis of the final product showed that different carbon nanostructures, such as MWCNTs, onion-type fullerenes, and nanospheres, could be obtained (using RSWT and ferrocene as a catalyst). The synthesis in quartz tubes under reduced pressure showed the formation of two phases, a solid powder and a film.

The results presented in this work show that carbon nanostructures can be obtained with the use of residual solid waste tires as a carbon source, which too is a possible solution to the problem of the disposal of waste tires.

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