

Composite Films from Polystyrene with Hydroxyl end Groups and Carbon Nanotubes

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Composites from polystyrene with hydroxyl end groups and multiwall carbon nanotubes were fabricated to evaluate their properties. The Carbon Nanotubes (CNTs) were synthesized by chemical vapor deposition technique using ferrocene and benzene as precursors. Polystyrene with hydroxyl end groups was prepared by solution polymerization employing styrene as monomer, 2-mercaptoethanol as chain transfer agent and AIBN as initiator. Thin films were obtained by two methods: pouring into petri dishes and dip-coating slides. CNTs were characterized to identify morphology and characteristic spectroscopic signals. The polystyrene with hydroxyl end groups and composites were analyzed by SEM, FTIR, Raman and UV-vis spectroscopies, Vickers microhardness and electrical resistivity. Raman analysis demonstrated chemical interactions between CNTs and polystyrene. Results showed that resistivity and transparency decreased by increasing CNTs concentrations in composites; transmittance was about 80% with 0.8 wt% content of nanotubes. The highest Vickers hardness registered value was at 1.6 wt% CNTs concentration.

Keywords: *carbon nanotubes, composite materials, polystyrene*

1. Introduction

Nowadays, the carbon nanotubes are widely studied materials due to their exceptional chemical and physical properties^{1,2}; by joining them with other materials these extraordinary characteristics can be transferred. Numerous researches look for interactions between carbon nanotubes and polymer matrices; CNTs dispersion into polymer matrices is a good method to provide electrical and enhanced mechanical properties to these macromolecules^{3,4}. The Van der Waals forces that usually agglomerate carbon nanotubes present an impediment to spread them into polymers⁵. Successful dispersion of nanotubes into polymers could be achieved through several chemical modification techniques by adding functional groups to CNTs^{6,7}. Common methods to prepare composites from carbon nanotubes and polymers consist of mixing the materials in a solvent that subsequently evaporates. Other authors achieved well results using the melt mixing technique⁸. This method is used in order to accomplish a physical and chemical interaction between the CNTs and the polymers; also were proposed as the most promising route on the preparation of polymer/CNTs composites⁹. Covalent bonding of polymer chains to CNTs plays an

important role in research and development on CNT-based materials¹⁰. Some researches were focus in the effect of pristine and functionalized carbon nanotubes in polystyrene (PS) matrices¹¹. A good dispersion of CNTs in PS thin films, produced by solution casting, was achieved by grafting the nanotubes surface with polystyrene chains¹². Spitalsky et al. remark that the excellent electrical properties of composites containing multiwall carbon nanotubes are promising for the design of low cost polymer composites for numerous future applications¹³.

Spectroscopy techniques, including Raman and Fourier Transform Infrared Spectroscopy (FTIR), are techniques that provide information for material characterization. Raman spectroscopy can identify carbon nanotubes and characterize different interaction types with polymers¹⁴; also has become one of the main characterization tools for CNTs due to the analysis of material quality, the microscopic structure of the tube and phonon and electron quantum confinement, data that could be acquired by other techniques, however they require time consuming or special sample preparations¹⁵.

The present research proposes the introduction of hydroxyl groups and the use of shorter chains of polystyrene matrices to form composites with carbon nanotubes. The CNTs were synthesized by Chemical Vapor Deposition (CVD) with

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laboratory conditions similar to those described on¹⁶; the nanotubes were obtained with a specific characteristic, OH functional group. The matrix modification, using short chains and the addition of OH functional groups in the polymer, represents a new focus on composite polystyrene synthesis, looking for a better interaction between carbon nanotubes and polymer molecules. The aim of this research was to incorporate CNTs into polystyrene with hydroxyl end group matrices, characterize the materials and evaluate their properties.

2. Materials and Methods

CNTs synthesis was performed by chemical vapor deposition into an experimental reactor based on¹⁶⁻¹⁸. Benzene (99.8%, Aldrich) and ferrocene (98%, Aldrich) were used as organic precursors, the second compound acted also as catalyst source. Reaction temperature was 760 °C; time process was 1 hour with 80 ml/min constant argon flow. Polystyrene with hydroxyl end groups (PSOH) was synthesized by solution polymerization according to Gutierrez et al.¹⁹, using styrene ($\geq 99\%$, Aldrich) as monomer, 2-mercaptoethanol (98%, Aldrich) as chain transfer agent and azobisisobutyronitrile (98%, Aldrich) as initiator. The polymerization took place under nitrogen atmosphere for 4 hours, with magnetic stirring at 450 rpm and 60 °C; this temperature value was applied to obtain short chain lengths.

Composites from PSOH and CNTs were obtained by mixing both materials inside a flask. The PSOH mixture with 0.2, 0.4, 0.6, 0.8, 1.6 and 3.2 wt% nanotubes concentrations were stirred at 1200 rpm during 20 min and settled in an ultrasonic cleaner (Branson 1510) afterwards. Two methods to produce composite films were used. For the first technique the slurry was poured into petri dishes and vacuum dried inside an Isotemp Vacuum Oven (282A) in order to obtain 100 μm thickness films. The second method to produce thinner composites films ($< 5 \mu\text{m}$) was using a digital immersion apparatus (E-ANT1; SK-UV). Slides were dipped at 20 cm/min for 5 seconds in the mixture.

In order to describe morphology of carbon nanotubes, Field Emission Scanning Electron Microscopy (FESEM) in a JEOL 7600 were performed. Scanning Electron Microscopy (SEM) in a JEOL JSM-IT300 characterized the polymer and the composites, the samples were coated with gold using a Denton vacuum sputter coater.

CNTs, PSOH and composites were analyzed by Fourier Transform Infrared Spectroscopy in a Tensor 27 Bruker. Raman Spectroscopy of nanotubes and PSOH were carried out in a MicroRaman DXR Thermo Scientific (solid state laser 532 nm with 30 samples exposures). An Ultraviolet - Visible spectroscope Mprobe UV-visNIR Semiconsoft examined the PSOH and composites; to perform the observation the films were placed without previously preparation upon a base to analyze thin films.

To acquire the material resistance, the composites were cut to form 0.5 cm² rectangular areas (1 cm x 0.5 cm) and the measurements were taken positioning the tip at the shorter length with a Multitester Steren - Mul600. PSOH and all composites concentrations were indented, 4 times by charge, with 0.001, 0.003, 0.005, 0.01 and 0.025 kgf forces by a Mitutoyo Micro Vickers Hardness Tester.

3. Results and Discussion

3.1. CNTs

FESEM micrographs showed carbon nanotubes blocks with diameters around 60 nm and lengths up to 40 μm (Figure 1a and b). The EDS analysis demonstrated that the carbon content in atomic percentages were 97.4, oxygen 2.3 and iron 0.3%. The oxygen percentages could be explained by the presence of OH functional groups on MWCNTs corroborated by FTIR.

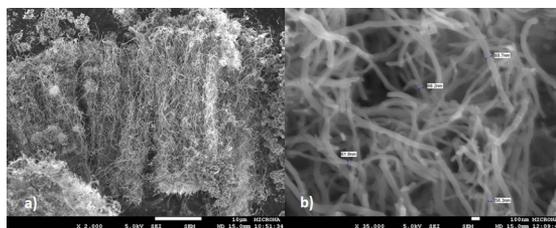


Figure 1. FESEM Micrographs: a) CNTs blocks, b) CNTs diameters.

CNTs FTIR spectra signals (Figure 2a) at 3051 cm⁻¹ correspond to the CH₂ stretch in aromatic rings²⁰, around 2890 cm⁻¹ to CH₂ and CH₃ vibrations, common to CNTs obtained by CVD^{21,22}. Bands on the 1750 - 1550 cm⁻¹ region have been assigned to C=C in aromatic rings²³. Furthermore the typical CNTs signals, the intensity that corresponds to OH functional group around 3500 cm⁻¹ was found.

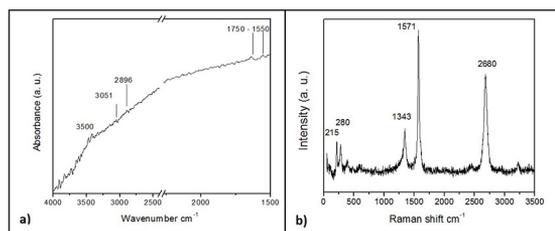


Figure 2. CNTs spectra: a) FTIR, b) Raman.

The Raman spectra (Figure 2b) confirmed CNTs characteristic bands for Multiwall Carbon Nanotubes (MWCNTs). G band reported for graphite like materials at 1571 cm⁻¹, D band assigned to defects in carbon nanotubes at 1343 cm⁻¹ and the G' band, at 2680 cm⁻¹, assigned to the first overtone of D mode²⁴⁻²⁶. Belin and Epron²⁴ reported

that the signals around 200 cm^{-1} correspond to the radial breathing mode of single wall carbon nanotubes, suggesting also their presence, however the D band width indicates that the principal structures are MWCNTs. The ID/IG ratio was 0.31, this result allows comparing the structural defects in MWCNTs and a higher relation suggests imperfections on the structure, related to sp^3 hybridizations^{27,28}.

3.2. PSOH and Composites

SEM images of PSOH and composites are shown in Figure 3. The micrographs showed a uniform polymer surface (Figure 3a). A subsequent analysis of composites demonstrated that despite the CNTs concentration increase, no carbon nanotube presence was observed on their surfaces, upper and lower ends. Figure 3b showed a covering surface of the composite, MWCNTs are focused, a similar picture was observed from the other side, demonstrating that the CNTs were dispersed inside the composites, like a natural sandwich structure. This behavior could be related to the affinity of the matrix and filler materials.

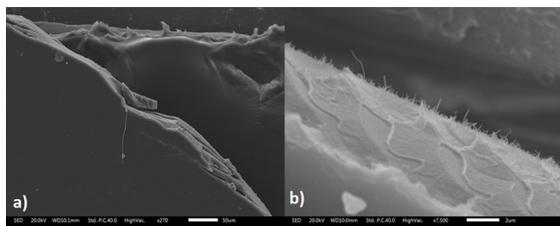


Figure 3. SEM micrographs: a) polymer surface, b) sandwich arrangement.

FTIR spectra of polystyrene with hydroxyl end groups and composites are depicted in Figure 4a. The 3077 , 3058 and 3026 cm^{-1} bands correspond to C-H vibrations in aromatic rings. Asymmetric and symmetric tensions of CH_2 were observed at 2923 and 2850 cm^{-1} . The 2000 - 1672 cm^{-1} region corresponds to the aromatic monosubstituted ring overtone bands. The signals at 1601 and 1493 cm^{-1} were assigned to aromatic C=C stretching. These bands are characteristic to conventional polystyrene²⁹⁻³¹. Additionally the spectra showed a broad band at 3462 cm^{-1} due to OH interactions^{19,20}. FTIR composites spectra, from 0.2 to $0.8\text{ wt}\%$ CNTs concentrations (Figure 4a), did not show band displacements of polystyrene with hydroxyl end groups. However interactions in the composites could be present. Hoult et al. suggest that the change of absorption intensities is related to films thickness variations³².

Figure 4b shows the UV-vis spectra for PSOH and 0.8 , $3.2\text{ wt}\%$ CNTs PSOH composites. Similar transmittance values, near 80% , were obtained from polystyrene with hydroxyl end groups and PSOH composites with $0.8\text{ wt}\%$ CNTs. A 40% transmittance value was reached with the highest CNTs concentration composite. Increasing CNTs

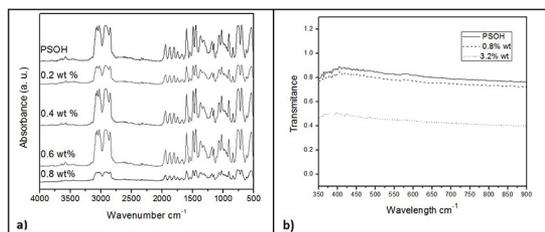


Figure 4. PSOH and composites spectra: a) FTIR, b) UV-vis.

concentration in PSOH composites, transparency decreases. Liu et al. have mentioned the effect on materials optical properties by CNTs concentrations and film preparations³³. The transmittance value is related to transparency on the films, a constant behavior through several wavelengths (350 - 900 nm) can open the door to multiple applications for these composite films.

The pristine PSOH Raman spectra (Figure 5a) show a strong and sharp peak at 1000 cm^{-1} , assigned to the ring breathing mode. The signal around 1300 cm^{-1} corresponds to the benzene trigonal deformation. The intensities corresponding to the CH stretching and to C-C stretching mode in aromatic rings were located at 1602 cm^{-1} and 3052 cm^{-1} respectively^{34,35}.

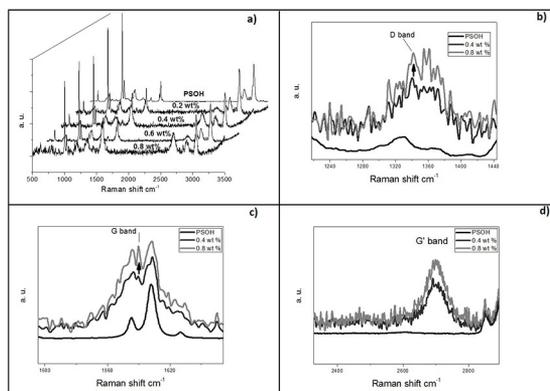


Figure 5. Raman spectra: a) PSOH and composites, b) D band appearance, c) G band appearance and displacement, d) G' band appearance and displacement.

The composites Raman (Figure 5a) spectra have similar appearance to the previously described; notwithstanding, the CNTs incorporated added and displaced some of the signals. The intensity around 1589 cm^{-1} , that correspond to the G band on carbon nanotubes (Figure 5c), appeared and showed a displacement of 18 cm^{-1} in comparison to the pristine CNTs. The D band intensity emerged and increased for the composites as is shown in Figure 5b, these behaviors are related to the introduction of covalently bound moieties on the CNTs framework³⁶. The D band intensity for the higher concentration were found at 1343 cm^{-1} and two signals (1355 cm^{-1} and 1361 cm^{-1}) with higher intensities appeared, originated from an intervalley double resonance

process³⁷. The G' band appeared in composites at 1698 cm⁻¹, presenting the same displacement that G band (Figure 5d). The enhanced ID/IG ratio (0.49), found on the composites spectra, in comparison to the pristine carbon nanotubes suggest higher structural defects²⁷; thus is indicative of possible CNTs covalent bonding with polymer through interactions between OH functional groups of the multiwall carbon nanotubes and the PSOH²⁸.

Pristine PSOH is an electric insulator; however, the addition of CNTs provided a decrease in resistance to composite films. The resistivity was calculated according to:

$$\rho = R \frac{S}{l}$$

where "R" is the electrical resistance (Ohms), "S" is the cross-sectional area (m²) and "l" is the composite film length (m). The resistivity composite values with 0.2 to 0.8 CNTs wt% concentrations were 48.7, 12.8, 6.3 and 3.2 Ω•m, respectively (Figure 6). This behavior could be for the contribution of the sp² carbon-carbon bonds, a higher concentration allows more contact between carbon nanotubes and the current passes more freely. For films with 0.8 CNTs wt% the electrical resistance was higher than the ones obtained by Jung et al.³⁸ with super aligned carbon nanotubes used as transparent heaters.

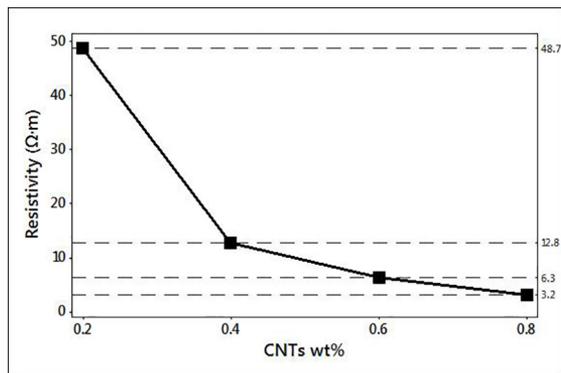


Figure 6. Composites resistivity behavior according to CNTs addition.

Energy dispersion for 0.005 kgf indentation can be appreciated in Figure 7. Several halos were formed with 0.4 CNTs wt% composite, nevertheless plastic deformation energy was better dispersed with a 3.2 CNTs wt% concentration. Data was collected for analysis of variance (ANOVA). Hardness was selected as response variable, composites nanotubes concentration (wt%) and loads were chosen as factors. Results showed an enhanced hardness through force increments, reaching an average of 30 HV (Figure 8a). Figure 8b shows hardness fluctuation in composites at different CNTs concentrations; the highest HV value was at 1.6 wt% of carbon nanotubes in composites, demonstrating

a similar behavior to Yang et al. that work with CNTs and conventional polystyrene³⁹.

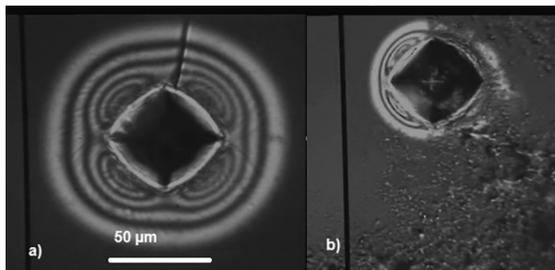


Figure 7. Vickers 0.005 kgf indentation: a) 0.4 CNTs wt%, b) 3.2 CNTs wt%.

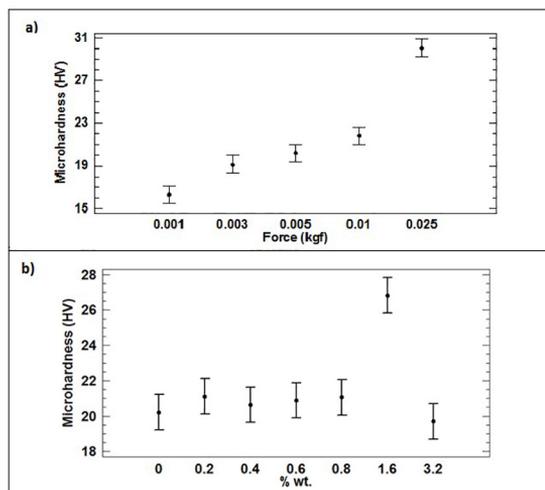


Figure 8. ANOVA results, hardness as response variable, factors: a) force, b) CNTs wt%.

4. Conclusions

Thin composite films were obtained through carbon nanotubes and polystyrene with hydroxyl end groups. SEM micrographs showed that CNTs were dispersed inside the composites, like a natural sandwich structure, demonstrating the affinity of the PSOH matrix and carbon nanotubes. Raman analysis demonstrated chemical bonding between MWCNTs and PSOH. The PSOH-CNTs composites mechanical, optical and electrical properties vary with different CNTs concentrations. Carbon nanotubes provided electrical conductivity to the PSOH films. Composite films electrical conductivity was increased depending CNTs percentages addition. The UV-vis spectra indicated a decrease in transparency according to CNTs concentration increase. Optical micrographs of Vickers indentations on composites demonstrated an increment in resistance to deformation with higher CNTs concentration, 1.6 CNTs wt% showed the best hardness results. This research represents a new focus producing composites using a short chains polystyrene matrix with OH functional groups and

CNTs, with OH group, to enhance their chemical interaction, opening the door to some future applications.

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