

---

**Development of PS/Multi-Walled CNT nanocomposite and characterization**

*Carreño-Márquez J.<sup>b\*</sup>, Zaragoza-Contreras A.<sup>a</sup>, Hernández-Escobar C.<sup>a</sup>, Mendoza-Duarte M.<sup>a</sup>, Román M. and Flores-Gallardo S.<sup>a</sup>,*

<sup>a</sup> Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua 31109, Chihuahua, Chihuahua, México.

<sup>b</sup> Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Avenida Universidad S/N, Chihuahua, Chihuahua, México.

---

**Abstract**

Polymerization of styrene was performed by dispersing multi-walled carbon nanotubes using miniemulsion polymerization technique varying the amount of surfactant used in the dispersion phase. Through the applied methodology a genuine dispersion was achieved modifying the properties of the original matrix. The resulting nanocomposite was characterized by Thermogravimetric Analysis, Differential Scanning Calorimetry and Dynamical Mechanical Analysis to determine the effects of nanotube inclusion on the mechanical and thermal performance of the composite. Impedance spectroscopy was achieved to find out whether or not some material acquired the capacity to conduce electrical flux. The obtained results indicated the formation of a strong nanotube – polystyrene interfacial interaction; besides, it was found that some composites presented electrical conductive properties, which was attributed to an efficient dispersion process.

**Keywords:** Nanocomposite, Multi-Walled Carbon Nanotubes, Characterization

---

**Contact:**

I. Jalil Anton Carreño-Márquez  
E. Armando Zaragoza-Contreras  
E-mail: [jalilcarreno@hotmail.com](mailto:jalilcarreno@hotmail.com)  
[armando.zaragoza@cimav.edu.mx](mailto:armando.zaragoza@cimav.edu.mx)

**Introduction**

Carbon nanotubes (CNTs) were discovered in 1991 by Sumio Iijima<sup>1</sup> and since then they have been of great interest due to their potential applications in different fields of science and technology. CNTs present a desirable combination of mechanical, electrical and thermal properties that no other materials have shown before<sup>2</sup>. The development of nanocomposites polymer/CNTs has been focused on the improvement of mechanical and electrical properties of the matrix<sup>3,5</sup>; however, CNT must be dispersed within the matrix in order to break the CNTs agglomerates which obeys to strong attractive van der Waals forces<sup>6,7</sup>, and design a medium that can provide affinity between CNTs and the matrix. Several strategies have been employed to improve CNTs dispersion into polymer matrixes<sup>8-10</sup> with different results. Several works have shown that *in situ* polymerization is a reliable strategy to obtain CNTs–polymer nanocomposites<sup>11,12</sup>, particularly miniemulsion polymerization, which provides the proper conditions to integrate the nanoparticle and the matrix into a compound<sup>13-16</sup>. In the case of CNTs the aspect ratio (length / diameter) makes quite complicated the encapsulation of these into polymer particles; the length of a CNT could be as long as some hundreds of nanometers and the size of the polymer particle is just a small fraction of the NTC length. Reports have shown that the interaction between CNTs and polymer particles, in nanocomposites obtained by *in situ* polymerization in dispersed media has been mainly superficial; in other words, the polymer particles stick to the surface of the nanotube<sup>7,17</sup>.

## Experimental

### Materials

Multi-Walled CNTs were synthesized by CVD technique using ferrocene and toluene, no treatment was given to the CNTs. Styrene monomer was distilled under vacuum before polymerization; anionic surfactant Triton-165 and Triton-305 were used as delivered; free radical initiator azobisisobutyronitrile was recrystallized from methanol. The water used was tridistilled quality.

### MWCNT-Polystyrene Nanocomposite Synthesis

Polystyrene/Multi-Walled CNT synthesis was performed by microemulsion polymerization, the procedure was the following: First, Multi-Walled CNTs were dispersed in 20 mL of styrene monomer in ultrasound for 15 min. The surfactants were added to the solution little by little; afterwards AIBN was added and dispersed in the emulsion for 5 min. Ultrasound was applied continuously so as to avoid as much as possible nanotube reagglomeration. The resulting emulsion was heated in the reactor at 70°C and a nitrogen atmosphere. The polymerization reaction allowed 8 h to be completed. Three different charges of CNTs were used (0.05, 0.1 and 0.2 g) besides of a blank or control of polystyrene without MWCNTs.

## Results

Thermogravimetric curves (TGA) of neat PS and Pst-CNTs composites with three different concentrations of CNTs (0.05, 0.1 and 0.2 %wt) are given in Figure 1. Thermal decomposition of each sample takes place in a programmed temperature range of 20 – 600 °C. In the case of neat PS the decomposition starts at 288 °C and is complete at a temperature of 425 °C, which indicates that the thermal stability for pure PS is higher. For the different PS-CNTs composites a behavior similar respect to neat PS is observed. These results suggest that the CNTs did not improve the thermal stability of composites.

Figure 2 shows the glass transition temperature ( $T_g$ ) obtained for Differential scanning calorimetry. Neat PS exhibits a glass transition temperature at 69.5 °C. Nanocomposites (PS-CNTs) with the two lowest CNTs concentrations (0.05 and 0.1 Wt. % of CNTs) has a lower glass transition temperature of 63 and 67 °C, respectively. However, PS-CNTs (0.2 wt % of CNTs) exhibit a higher glass transition temperature found at 72 °C respect to neat PS. These results can be explained as follows. It is quite possible that the addition of CNTs to a polymer matrix to lower concentrations increase the free volume between polymer chains, allowing the particles act as plasticizer in the matrix polymer. On the other hand, the increase in CNTs concentrations improves the interactions Polymer – CNTs.

Figure 3 and 4 shows dynamic mechanical behaviour of the neat polystyrene and PS-CNTs nanocomposites with respect to temperature. We can see that the storage modulus (Figure 3) remains almost same for a long range of temperature, then decreases sharply and levels off. The region at which the sharp decrease is shown is the glass transition temperature of the material. All the curves show an improved storage modulus ( $E'$ ) values at the initial region compared to the neat polystyrene. The composites were prepared with NTCs and the matrix - NTCs interaction is responsible for the increase in storage modulus.

Loss modulus ( $E''$ ) curves of the polystyrene nanocomposites at a frequency of 1 Hz are shown in Figure 4. The peak in the curves corresponds to the glass transition temperature of the composites. We can see that the  $T_g$  values shifted to the right hand side for the composites upto 0.2 wt %. This positive shift is attributed to the better NTCs - matrix interaction. However, the 0.05 and 0.1% NTCs composites showed negative shift from the neat PS. This anomalous behaviour is believed to be due to the agglomeration of the filler particles thereby reducing the better filler matrix interaction.

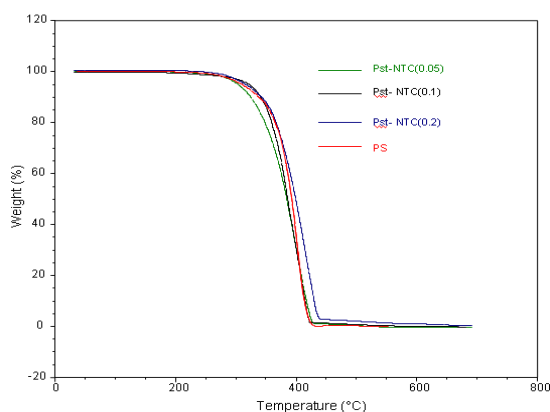


Figure 1. ThermoGravimetric Analysis of PS and MWCNT/PS composites

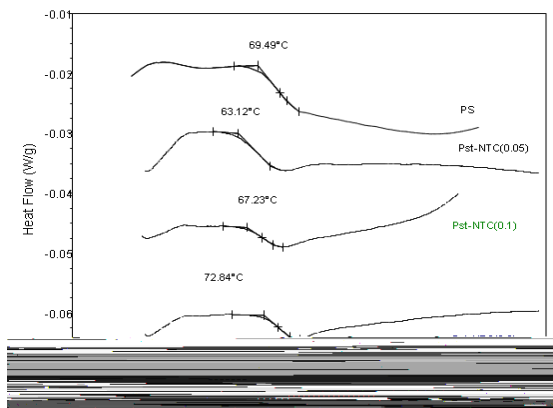


Figure 2. Differential Scanning Calorimetry of PS and MWCNT/PS composites

Figure 3 Dynamical Mechanical Analysis (DMA)  
Plastic Module

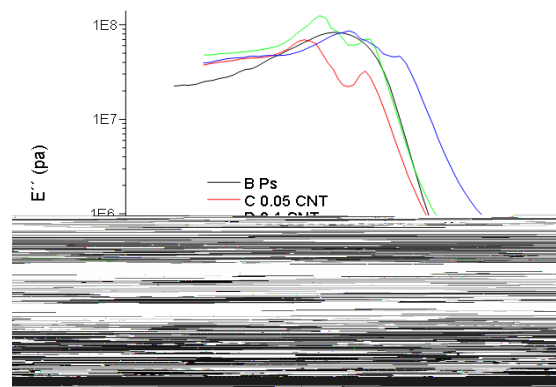


Figure 4. Dynamical mechanical Analysis (DMA)  
Viscous Module

#### Acknowledgement

Thanks to Miguel Orozco, Guerrero Mendoza and Daniel Lardizabal for their helpful attendance during this research.

## References

1. Iijima Sumio. Nature (1991). Vol. 345. 56-58.
2. Coleman JN et al. Carbon (2006), 44, 1624-1652
3. Gojny FH, et al. Polymer (2006), 47, 2036-2045
4. Eitan A, et al. Comp Sci Tech (2006), 66, 1162-1173
5. Hill DE, et al. Macromolecules (2002), 35, 9466-9471
6. Park SJ, et al. Curr Appl Phys (2005), 5, 302-302
7. Sandler JKW, et al. Polymer (2003), 44, 5893-5899
8. Shen J., et al. Polymer (2005), 46, 5218-5224
9. Xie, X-L; et al. Mat Sci Eng R (2005), 49, 89-112
10. Lee IS, et al. Diam Rel Mat (2006) 15, 1094-1097
11. Funck A, and Kaminsky W, Comp Sci Tech (2007), 67, 906-915
12. Zhao C, et al. Polymers (2005), 46, 5125-5132
13. Tiarks F, et al. Macromol Chem. Phys. (2001), 202, 51-60
14. López-Martínez EI, et al. J. Polym. Sci. Part B: Polym. Phys. (2007), 45, 511-518
15. Zhang S-W, et al. Langmuir (2005), 21, 2124-2128
16. Erdem B, et al. Macromol. Symp. (2000), 155, 181-198
17. Vandesvorst P, et al. Prog Polym Coat (2006) 57, 91-97
18. Yu Y, et al. Synthetic Metals (2005), 150, 271-277