PLASMA MODIFICATION AND DISPERSION OF MULTIWALLED CARBON NANOTUBES (MWCNT) IN HIGH IMPACT POLYSTYRENE BASED NANOCOMPOSITES: ANALYSIS BY ELECTRON MICROSCOPY (TEM AND SEM)

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Recibido: Septiembre 2013. Aprobado: Julio 2014.
Publicado: Noviembre 2014.

ABSTRACT

The present work is focused on the synthesis and preparation of high impact polystyrene (HIPS)/Multiwalled carbon nanotubes (MWCNT) composites and their characterization and analysis by transmission and scanning electron microscopy (TEM and SEM). Specifically, the analysis consists in evaluate the effect of volume fraction of elastomeric phase (Φ) in the HIPS on the threshold percolation concentration (Pc). The MWCNT were modified using a plasma reactor in presence of styrene, while the HIPS were synthesized in a batch reactor by mean of the mass-suspension technique. HIPS and MWCNT modified were mixed in melt at different concentrations of MWCNT. Finally, all materials were analyzed by SEM and TEM. A polystyrene (PS) thin layer (2-4 nm) on the MWCNT was found by TEM. On the other hand, the HIPS morphology salami type was observed for all HIPS synthesized with an average particle diameter (Dp) from 1.4 to 1.8 μm and a Φ from 0.35 to 0.40. Respect to the 3D continuous network of MWCNT builds (percolation threshold) was found at 3 and 2 wt-% of MWCNT. Decrease in the Pc was attributed to the increment in the Φ. That is, the rubber particles act as big holes into the three-dimensional continuous network, and if the amount of particles in volume increases the MWCNT concentration necessary to form the network decreases. Finally, the thin layer of PS on nanotubes surface plays an important role, it avoids the agglomeration of MWCNT´s and allows a good dispersion of the MWCNT in the PS phase.

Keywords: Nanocomposites, carbon-nanotubes, polystyrene, plasma-modification, morphology

MODIFICACION POR PLASMA Y DISPERSION DE NANOTUBOS DE CARBONO DE PARED MULTIPLE (MWCNT) EN POLIESTIRENO DE ALTO IMPACTO: ANALISIS MEDIANTE MICROSCOPIA ELECTRONICA (TEM Y SEM)

RESUMEN

El objetivo del presente trabajo fue sintetizar y preparar compuestos base poliestireno de alto impacto (HIPS)/Nanotubos de carbono de pared múltiple (MWCNT), y su caracterización y análisis mediante microscopía electrónica de transmisión (TEM) y de barrido (SEM). Se estudió el efecto de la fracción volumen de la fase elastomérica (Φ) en los HIPS sobre la concentración crítica de percolación (Pc). Los MWCNT se modificaron utilizando un plasma-reactor en presencia de estireno, posteriormente se sintetizaron los HIPS mediante la técnica de masa-suspensión. Los HIPS y MWCNT se mezclaron en fundido utilizando diferentes concentraciones de MWCNT, todos los materiales obtenidos se analizaron mediante TEM y SEM. En los MWCNT modificados se encontró una capa delgada (2-4 nm) de poliestireno (PS). En los HIPS sintetizados se observó una morfología de tipo salami con un diámetro de partícula promedio (Dp) de 1.4 a 1.8 mm y una Φ de 0.35 a 0.40. La Pc se alcanzó a concentraciones de 3 y 2 % en peso de MWCNT. La disminución de Pc se atribuyó al aumento en Φ, es decir, las partículas de hule actúan como grandes hoyos dentro de la red tridimensional continua de MWCNT, y si la cantidad de partículas en volumen (Φ) se incrementa, la concentración de MWCNT necesaria para formar una red continua disminuye considerablemente. Finalmente, la delgada capa de PS en la superficie de los nanotubos juega un papel de suma importancia, esta evita la aglomeración de MWCNT y permite una buena dispersión de los MWCNT en la fase de PS.

Palabras claves: Nanocompuestos, nanotubos de carbono, poliestireno, plasma, morfología

INTRODUCTION

In the last few years the investigation on the matter at nanometric scale has been arising exponentially [1]. Because, the matter at dimensions less than 100 nm (nanoparticles), presents different and/or new properties, never seen in its macroscopic form. The control in size and form of the matter, at nanometric scale, has avoiding the development of the nanotechnology. It was reflected in the creation of new materials with new properties. Nanoparticles can be incorporated to other materials such as ceramics and polymers; it brings properties transference from the nanoparticles to the matrix. For example, polymeric conductive composites can be obtained by mean of the incorporation of Au, Ag, Al, Cu or C nanoparticles [2]. Factors to determine the efficiency of the nanoparticles are: chemistry nature, size, geometry (wire, tubes, rods, spheres, cubes, platelets, etc) and the aspect ratio (defined as the longitude/diameter or side ratio). Other important parameter to establish a better performance of the nanoparticles is the dispersion improvement by means of the surface modification. For the carbon nanotubes (CNT), discovered by Iijima in 1991 [3], its alignment and the intercalation in a polymer system constitute important factors to better performance [4].

Several works in the literature report studies about polymer continuous phase/MWCNT, it results in an electrically conductive mixture, at 5 wt-% or more of CNT concentration [5]. However, higher concentrations may cause a decrease in the mechanical properties. On the other hand, using multiwalled carbon nanotubes (MWCNT) in a polymeric matrix increases durability, tensile strength and flexibility and diminishes the weight [6].

Meincke *et al.* demonstrated that a nanocomposite of polyamide 6/ABS and 3 % of NTC conduces electricity, in addition by the first time there was demonstrated the double percolation phenomenon, that consists in a PA/6 percolated phase and a three-dimensional continuous network [7].

According to the above, this work is focused in the formulation of nanocomposites base of high impact polystyrene, HIPS (heterogeneous system constitutes by a polystyrene continuous phase and a polybutadiene rubber disperse phase) and multiwalled carbon nanotubes. Specifically, it deals to evaluate the volume fraction of rubber variation in the HIPS on the Pc.Leave one blank line before and one blank line after each table.

MATERIALS AND METHODS

Materials

Styrene (S) supplied by Poliformas S. A. polybutadiene (PB) DIENE 40 synthesized by Dynasol Elastomeros S. A. de C. V., polystyrene (PS) with Mn of 103 (PS_1) and 66 (PS_2) kg/mol by Resirene S. A. de C. V. and benzoyl peroxide (BPO) from Aldrich, were used to synthesize HIPS. MWCNT by CheapTubes Inc. and osmium tetroxide (OsO_4) by Aldrich were used to prepare nanocomposites and to stain HIPS and nanocomposites samples, respectively.

Methods

Plasma MWCNT modification was carried out in a plasma reactor, where the styrene monomer was polymerized in the vapour phase, and deposited in the MWCNT surface. The plasma reactor was designed by Ramos *et al.* [8] and consists of a power controller coupled to a radiofrequency generator RFG (Advance Energy RFX600) of 13.76 MHz, vacuum pump, a flux control valve and a 500 mL round bottom flask. The last one is held on an electrical heater with constant stirring to improve a homogeneous PS coating on the MWCNT surface. A copper wire that acts as an electrode is coiled around the round bottom flask and one of the ends of the wire is connected to the RFG, 2 g of MWCNT were introduced in the glass flask at an internal pressure of 4.5 mbar (using the vacuum pump). Then, the styrene monomer flow was fixed at 0.15 cm^3/min. The MWCNT were treated for 60 min at intensity of 100 W.

To synthesize HIPS, a 4 L steel reactor (by Paar), disposed with an anchor-turbine stirrer was used. In a first step, 8 wt-% of PB and/or 5 wt-% of PS were solved in styrene monomer (S), after 12 h, 0.1 wt-% of BPO was added. The pre-polymerization step was done at 90°C and the evolution of the conversion fraction (X) was followed to a value of 0.25 in order to reach the HIPS morphology establishment (at a phases inversion phenomenon) for the three HIPS synthesized. In a second step, the reactant blend is followed by means of suspension method to total conversion fraction. The components and concentrations for the three different formulations are shown on Table 1.

Preparation of the nanocomposites base HIPS/MWCNT was carried out in a melt mixer CW Brabender ATR disposed with a 70 cc mixing chamber at 200°C and 60 rpm, the residence time was 12 min. For each HIPS synthesized 0.6, 0.8 1, 2, and 3 wt-% of MWCNT, previously plasma modified, were used.

TEM, STEM and SEM characterization

All nanocomposites and reference HIPS were cut using a Leica Ultracut ultra-microtome (at cryogenic conditions). All samples were stained using OsO_4 for phase contrast [9]. The samples of the MWCNT modified, reference HIPS morphology and the HIPS/MWCNT, were observed in a transmission electron microscope field emission FEI Titan 80-300 kV, operated at 300 kV, with a resolution point-to-point of 1Å in HRTEM and 1.4Å in STEM, and finally, using a scanning electron microscope JEOL the dispersion state of MWCNT in the PS matrix of HIPS was analysed.

Table 1. High impact polystyrene recipes and relate morphology parameters.

HIPS	wt-%				Dp (nm)	Φ
	S	PB	PS_1	PS_2		
H1	92	8	-	-	1.4	0.35
H2	87	8	5		1.7	0.39
H3	87	8	-	5	1.8	0.40

RESULTS AND DISCUSSION

MWCNT modification

MWCNT modified by styrene plasma in vapor phase are shown in Figure 1. A thin layer of PS (4 nm) on the surface of MWCNT is observed as a consequence of the plasma treatment, it can be differenced of the nanotube carbon walls, because, it not have crystalline order, it is amorphous carbon, while the carbon nanotubes walls have high crystalline order, it is demonstrated by FFT analysis in the Figure 1c.

The plasma treatment creates free radicals on the MWCNT surface [8] and the monomer molecules (styrene) polymerized on the surface forming a polystyrene layer. This layer will be as an anchorage between PS matrix and MWCNT to improve the interfacial adhesion and to avoid the formation of clusters of MWCNT to reach the Pc at lower concentration. The layer is not homogeneous, however it is situated along the MWCNT (see Figure 1a and b).

HIPS morphology

As was described in the experimental section the morphology and related parameters of the different HIPS were observed and calculated by TEM. The morphology for all HIPS synthesized was shown in the Figure 2, they have salami-like morphology, it constitutes of PB (clear section in the STEM images) and multi-occluded PS drops (dark section in the STEM images). All of them disperse in a continuous PS phase (dark continuous section in the STEM image).

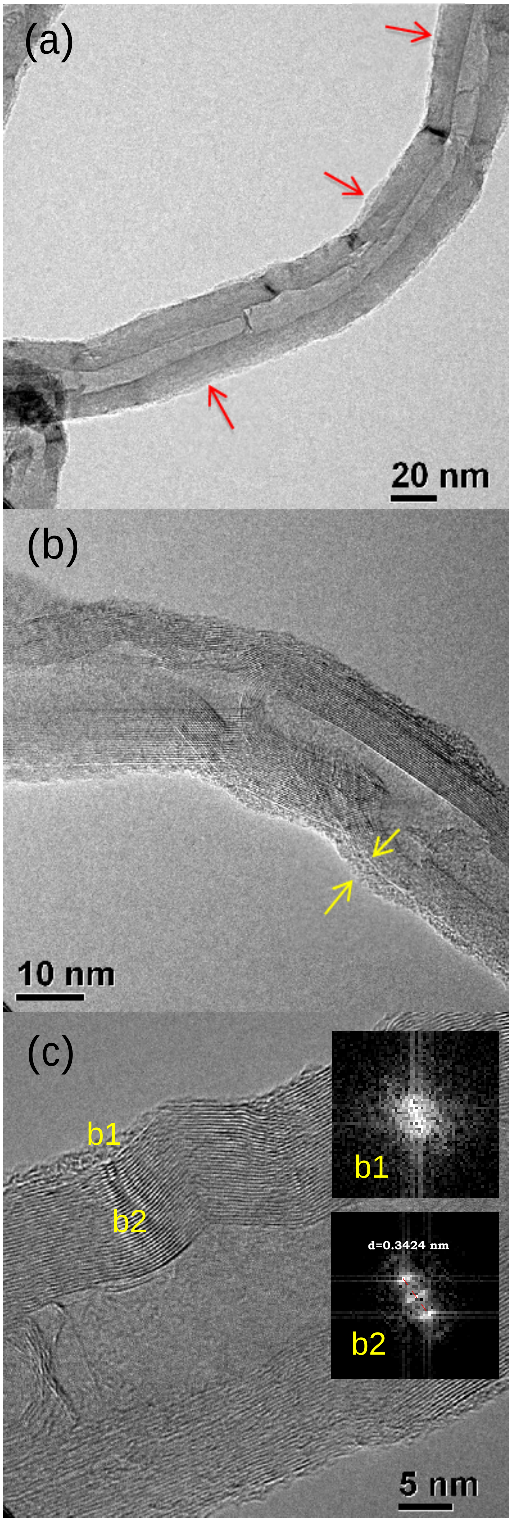

Fig. 1. TEM micrographs of MWCNT modified at: a) 80,000X, b) 250,000X and c) 300,000X and FFT.

The salami-like morphology is dominant however some core-shell structures are present. Figures 2b and 2c for HIPS H2 and H3, respectively, show larger particles than H1, approximately of 5 µm. Dp and Φ was determined by measuring more than 300 particles. For HIPS H1 Dp=1.4 µm, while H2 and H3 reaches values of 1.7-1.8 µm as shown in the Table 1. In case of Φ values an increase was also observed, from 0.35 in H1 to 0.40 in H3. This behaviour is attributed to the incorporation of 5 wt-% of PS at the beginning of the polymerization, it increases the repulsion forces between PB/S phase and PS/S phase, during the polymerization, because, PB and PS are incompatibles [10]. Baer also reported similar results in terms of an increase of Dp and Φ values [11].

HIPS/MWCNT base nanocomposites morphology

Figure 3 shows the images by TEM for HIPS: a) H1 with 3 wt-% of MWCNT, b) H2 with 2 wt-% of MWCNT and c) H3 with 3 wt-% of MWCNT. Samples analysed by TEM correspond at the Pc where the nanocomposites present a surface electrical resistance of 1x10^{9}, 1x10^{6} and 1x10^{7} Ohms.cm, respectively. These values are lower than the electrical resistance for the HIPS without MWCNT equal 1X10^{12} Ohms.cm [12]. The TEM analysis was made to corroborate the theory of site contacts [13], it establishes that each particle or nanoparticle in the polymeric matrix, in this case MWCNT, should be present an average contact number (M) major to the unit, to improve the electrical conductivity (reduce the electrical resistance) by mean of the built up of three-dimensional network. Some MWCNT fragments are observed in Figure 3a, it shows at least one contact or two (labelled by the numbers in the image). It´s so difficult to find a MWCNT extended, because the network formed is three-dimensional. However in the Figures 3b and c, several MWCNT with two or more contacts (labelled by the numbers in the image), were observed. The contacts in the three-dimensional network caused a significant decrease in electrical resistance at low concentration MWCNT composite that of a homogeneous matrix. It can be explained by the double percolation phenomenon [7], in its case the first percolation occurs at the morphology establishment, during the polymerization.

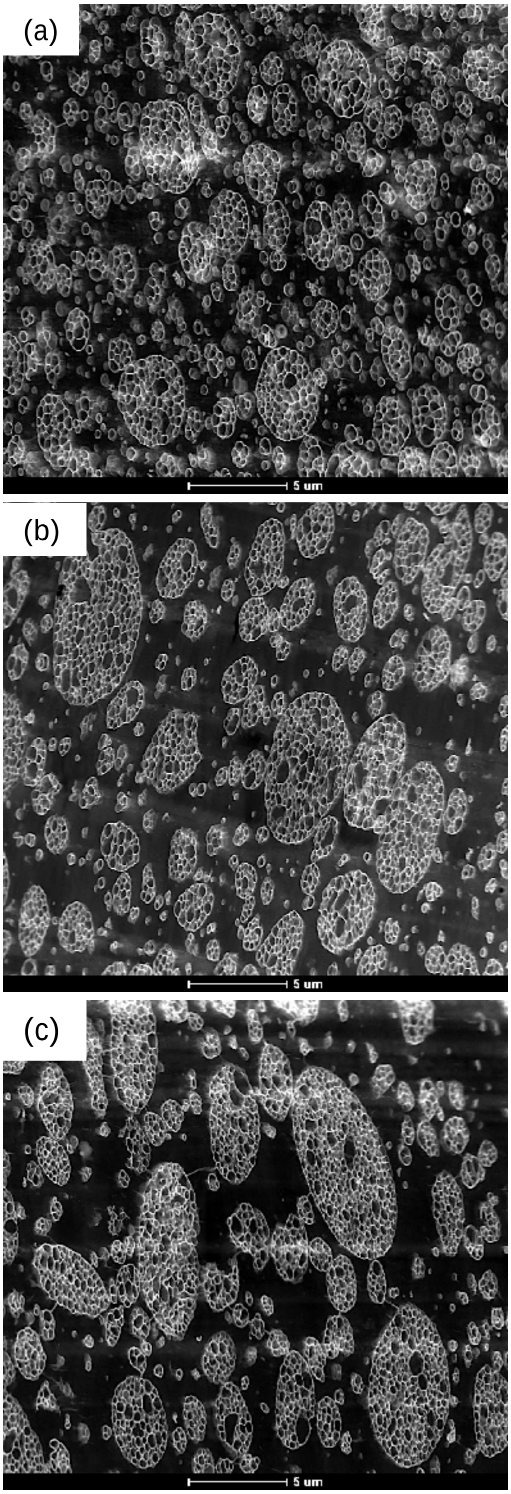

Fig. 2. Morphologies of HIPS: a) H1, b) H2 y c) H3.

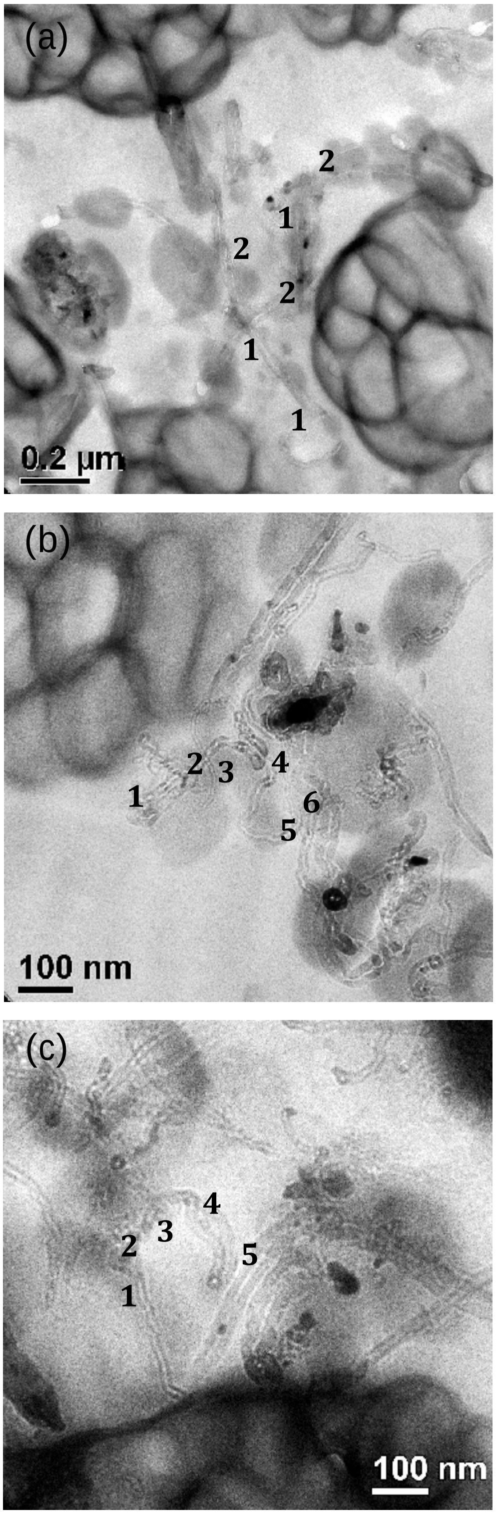

Fig. 3. Images by TEM of HIPS/MWCNT at different MWCNT concentration: a) H1 with 3 wt-%, b) H2 with 2 wt-% and c) H3 with 3 wt-%.

With the X evolution, the PS/S disperse phase became a continuous phase and the PB/S initial continuous phase became a disperse rubber phase (salami-like particles) (phases inversion phenomenon). A second percolation is due the formation of three-dimensional MWCNT network. The rubber salami-like particles act as big holes (1.4-1.8 μm) into the MWCNT network, this decreases the MWCNT concentration at Pc. This behaviour was not easy to observe at higher magnification, because the rubber particles are presented at micrometric scale and the MWCNT were observed as a dark spots surrounding the rubber particles as it can observed in the Figure 4.

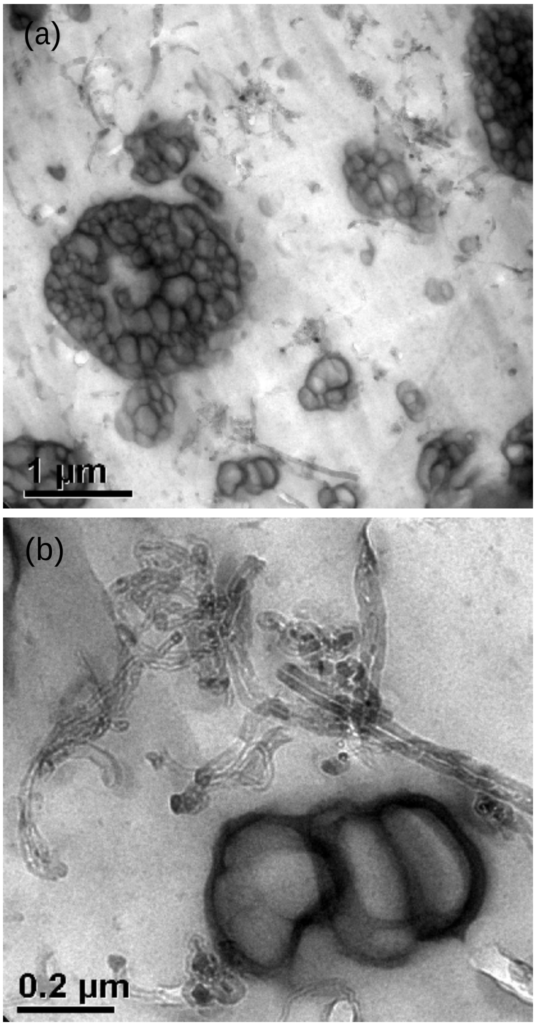

Fig. 4. TEM images for the nanocomposite H3 with 3 wt-% of MWCNT at a) 3800Xand b) 16500X

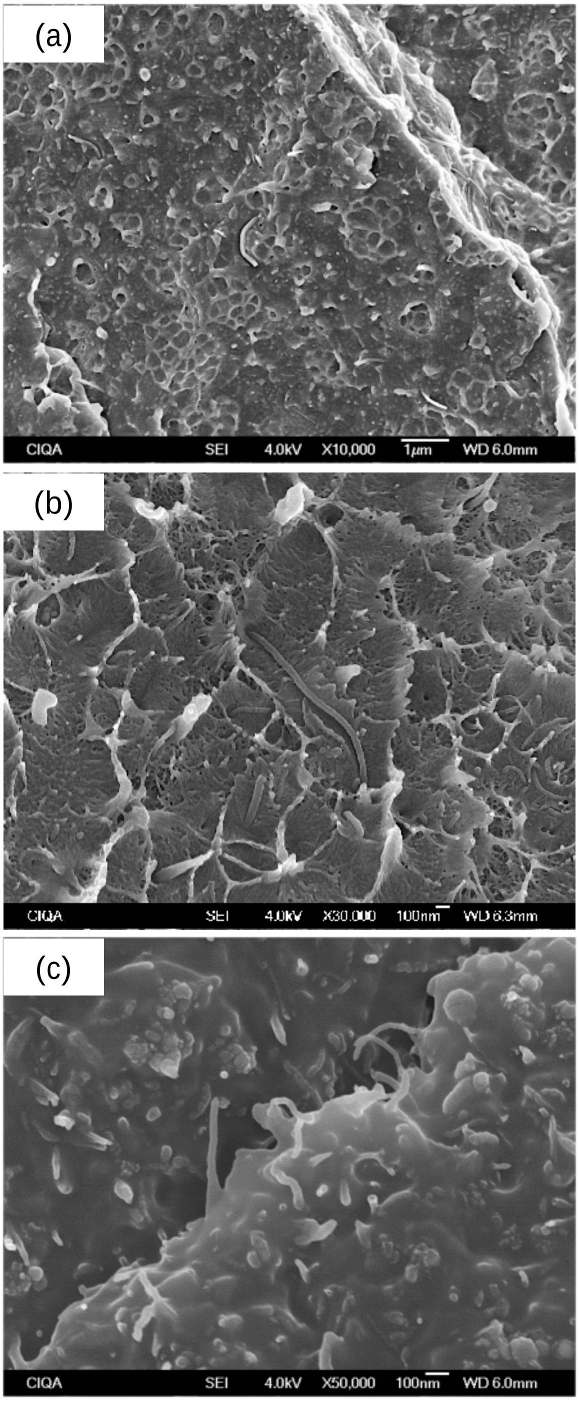

Fig. 5. Images by SEM of RX2CNT2 at a) 10000X (scale bar 1μm), b) 30,000X y c) 50,000X (scale bar 100 nm)

The MWCNT modified/HIPS nanocomposites were evaluated by SEM, these images are presented in Figure 5. In Figure 5a a good dispersion of rubber particles (salami-like particles previously stained) is observed, while the MWCNT was so difficult to distinguish at 10000X, however at 30000X (figure 5b) MWCNTs present a homogeneous dispersion, and a toughness fracture was observed.

Finally in Figure 5c the MWCNTs dispersed homogeneously in the PS matrix is observed. Both, toughness fracture and homogeneous dispersion were due to the low interfacial tension between PS and MWCNT as a consequence of the MWCNT plasma modification, it avoided the clusters formation.

CONCLUSIONS

Surface modification of the MWCNT was evidenced by FFT analysis and with the observation of the image acquired in the TEM. Homogeneous dispersion of MWCNT was observed by SEM and the HIPS/MWCNT composite presented a toughness fracture, when the PS matrix in HIPS is brittle. Both were attributed to the plasma modification of MWCNT. The M factor major to the unit was corroborated partially by TEM, at the Pc. The Pc decreases from 3 to 2 wt-% of MWCNT when the Φ was increased from 0.35 to 0.39.

ACKNOWLEDGMENTS

The authors would like to thank the Consejo Nacional de Ciencia y Tecnologia (CONACyT) for the financial support through the Project 156366. And thanks to Mónica A. Ceniceros, Miriam Lozano, Guadalupe Méndez, J. Guadalupe Téllez and Juan Uriel Peña for their technical support.

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