

SWNT-Filled Thermoplastic and Elastomeric Composites Prepared by Miniemulsion Polymerization

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ABSTRACT

SWNT-filled polystyrene (SWNT-PS) and styrene–isoprene (SWNT-SI) composites prepared by miniemulsion polymerization showed distinctive physical features such as uniform black coloration, high solubility in toluene as well as in tetrahydrofuran (THF), and semiconductor to ohmic electrical behavior. Raman spectra for both hybrid materials suggested a reduced vibrational freedom of the polymer chains as a consequence of the nanotube incorporation. An adsorbed polymer layer on the nanotube bundles contributes to a better dispersion of the inorganic nanoreinforcement.

Introduction. One of the several reasons that engineering research aimed toward the purification, functionalization, and incorporation of carbon nanotubes into polymeric matrices has been actively pursued for the past five years is that vastly important applications, from anticorrosion paints to nanometer-thick conductive thin films, are expected to have a direct impact on the world market worth hundreds of millions of dollars. Among the challenges introduced in the fabrication of nanotube-filled polymer composites is the necessity to creatively control and make use of surface interactions between carbon nanotubes and polymeric chains in order to obtain an adequate dispersion throughout the matrix without destroying the integrity of the nanotubes (NTs). Solution-evaporation methods have been the major experimental route to prepare both multiwall nanotube (MWNT) and single wall nanotube (SWNT) filled thermoplastics such as polystyrene (PS),¹ poly(vinyl alcohol) (PVA),² polyhydroxyaminoether (PHAE),^{3,4} poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene) (PmPV),⁵ as well as epoxy thermosets.⁶ Solution-casting methods have limited applicability for producing highly conductive films because SWNT composites tend to saturate at 1–2% nanotube content as the excess nanotubes aggregate.⁵ In addition, most polymeric materials need a large amount of solvent to be completely solubilized and consequently incorporate the NTs. These solvents are known organic liquids of high toxicity such as toluene, chloroform, tetrahydrofurane (THF), or dimethyl formamide (DMF).

Recently, inorganic fillers such as carbon black,⁷ titanium dioxide,⁸ magnetite,⁹ calcium carbonate,^{8–9} and silica¹⁰ have

been encapsulated by using the surfactant-enhanced miniemulsion polymerization technique. Herein, the inorganic material is first dispersed in a monomer and then the mixture is subjected to conditions of high shear typical of miniemulsification. Using either oil-soluble or water-soluble radical initiators under mild temperature conditions accelerates the polymerization, originating hybrid materials with different structures: encapsulated filler; polymer core with attached inorganic particles; or a mixture of both.¹⁰ A procedure similar to that used to create a doped polyaniline (PANI)-multiwall carbon nanotube composite under conditions of emulsion polymerization is presented by Deng et al.¹¹ They observed an increase in electrical conductivity of about 25 times between the PANI-NTs composite (10% load of NTs) with respect to the conductivity of the parent PANI. Another example of surfactant-aided composite fabrication employs a dispersion of carbon nanotubes in a cationic surfactant to generate comicelles that serve as a template for the synthesis of nanotube-containing silicon oxide microrods.¹²

In this paper, SWNT-PS and SWNT-SI hybrid materials have been prepared *in situ* under miniemulsion polymerization conditions, utilizing a cationic surfactant solution—slightly above the critical micelle concentration (CMC)—containing either 0.6% or 1.2% purified SWNT as the continuous phase. To prevent microdroplet coalescence and the Ostwald ripening effect, a hydrophobe (hexadecane) was mixed with the monomers prior to ultrasonication of the mixture. Seeding the monomer with a PS–AlCl₃ acid complex seemed to induce higher monomer transformation rates and consequently better incorporation of the nanotube inside the matrix. A similar procedure using the anionic surfactant sodium dodecyl sulfate (SDS) did not succeed in

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incorporating the nanotubes inside the polymeric matrix, and consistently only neat polymer and a dispersed nanotube solution were obtained. AC impedance and DC resistivity measurements performed on the SWNT-PS composites showed that nanotube content significantly modifies the electrical response of the parent matrix, and for the specific case of an 8.5% nanotube loading the resistivity value drops over 10 orders of magnitude.

Experimental Section. Surfactant–Nanotube Solution. The SWNTs employed in this study were purchased from Carboxene (batch CLAP 8256). This raw material was further purified according to a procedure described before,¹³ which ensures a carbon content in the final product of at least 86%. Cetyltrimethylammonium bromide (CTAB) from Aldrich and SDS (Aldrich, 98% purity) were added to separate vessels containing deionized water. The purified nanotube powder was weighed and added to the anionic and cationic surfactant solutions as to have nanotube contents of 0.6 and 1.2 weight percent. Mixing and moderate sonication (45 W) for 2 h yielded dark solutions of well dispersed nanotubes showing negligible amounts of precipitate.

Miniemulsion Polymerization. The inhibitors in both the styrene (99% purity, Aldrich) and isoprene (99% purity, Aldrich) monomers were removed by vigorously shaking a small volume of monomer (ca. 25 mL) with one gram of basic alumina (activity grade I, Sigma) in a 30-mL vial. A typical synthesis routine for the SWNT-PS composite is as follows: 0.8 mL of hexadecane (99.8% purity, Fisher) and 0.05 mL of PS–AlCl₃/hexadecane mixture were dissolved in 4 mL of styrene. A 0.05 g amount of an oil-soluble initiator (AIBN (99% purity, Aldrich)) was dissolved in 1.5 mL of pure ethanol (Absolute 200-proof, AAPER) and then mixed with 35 mL of the surfactant–nanotube solution. The monomer/hydrophobe/catalyst was added to the surfactant/nanotube/initiator solution and the whole volume shaken for 1 h at 200 cycles/min. Afterward, the vial content was sonicated for 60 s at room temperature with a Fisher 550 sonic dismembrator operating at the equipment amplitude setting of 5. As a result of the sonication, the solution turned into a gray-bluish emulsion without any traces of carbon deposits or other particulates. Immediately after sonication the sealed vials were transferred to a constant-temperature device operating at 65 °C and providing moderate shaking. Typically, the reaction was assumed to reach completion after 14 h. After this time the vials were opened and the whole contents poured into a large volume of pure isopropyl alcohol (J. T. Baker) where, for the samples employing CTAB, coagulation immediately took place.

SWNT-SI preparation followed a procedure similar to that of the SWNT-PS, with the only difference being that 2 mL of each monomer (styrene and isoprene) was used. After the reaction, the gray-bluish emulsion was coagulated, and instead of producing flocculated material as in the SWNT-PS, the larger SWNT-SI coagulates aggregated into a whitish rubbery solid. By way of comparison, the reference material (i.e., polystyrene and styrene–isoprene copolymer) was synthesized using the same anionic and cationic surfactant solutions and procedures described above, obviously without

adding the carbon nanotubes. In the case of the baseline polymers or reference materials, both cationic and anionic surfactants yielded polymers with similar characteristics. Polymerizations within SDS/SWNT solutions were not investigated any further, as in every case a clear polymer and a dark solution, presumably containing the nanotubes, separated as two different phases.

Solids Characterization. Raman laser spectroscopy was used to probe the structure of the unmodified polymers, as well as the SWNT-PS and SWNT-SI hybrid materials. In all cases an excitation wavelength of 514 nm with 35 mW intensity served to scan the spectral range between 80 and 4000 cm⁻¹. Other experimental parameters were: acquisition time = 1 min; lens power = 50×. Sample analysis in the solid state was preferred over the alternative method of dissolving the polymeric specimen in a solvent and then casting it over a glass slide. The former procedure gave stronger signals and presented less fluorescence problem. For AC impedance measurements (Solartron 1260 impedance analyzer) at room temperature, a two-probe geometry was employed. Disk-shaped parts of the SWNT-PS composite were compression-molded to different thicknesses and sandwiched between two polished copper electrodes (area = 4.908 cm²) held tight to the specimens by two flat polycarbonate plates. Fowler Associates Inc. (Moore, SC) carried out DC volume resistivity measurements in accordance with ASTM D-257, also on disk-shaped SWNT-PS molded specimens.

Results. Miniemulsion polymerization is a well-established method for producing particles with very narrow size distributions.¹⁴ This process has the advantage of requiring substantially less surfactant to stabilize the reacting hydrophobic droplets inside the aqueous medium, and eliminates the complicated kinetics of monomer transfer into micelles during a typical emulsion polymerization.

Although it is still not clear to us how cationic surfactants interact with SWNTs in order to stabilize monomer droplets during a typical miniemulsion polymerization experiment, we were able to prepare nanotube-filled polystyrene and styrene–isoprene copolymer with properties markedly different from those of the parent polymers. The reacted miniemulsion containing polystyrene-filled material (SWNT-PS) had a gray-bluish color, which after coagulation with 2-propanol decanted as a gray powder. This powder was filtered and washed several times with deionized water to remove any residual surfactant, and thereafter set overnight in a vacuum at 75 °C to drive off any unreacted monomer and moisture. With the drying operation the gray-colored powder turned into very hard black pellets. In contrast to the SWNT-PS, control samples of pure polystyrene were completely white after the drying period and had a characteristic powdery consistency. All evidence suggests that the initial load of nanotubes present in the surfactant/nanotube solution is incorporated into the reacted polymeric phase as the wash solution with isopropyl alcohol was clear and did not show any black precipitate.

Temperature programmed oxidation (TPO) measurements performed in SWNT-PS composites prepared with a starting

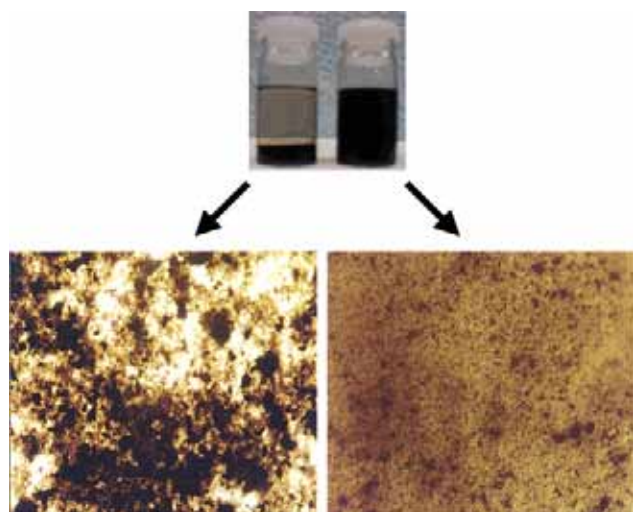


Figure 1. (top) Toluene suspensions of nanotube-filled polystyrene after three weeks. (left) Simple component mixing. (right) SWNT-PS pellets dissolved. (bottom) 100 \times transmission light micrographs of 30 μ m thick cast-films containing 8–9% weight carbon nanotubes, highlighting the formation of aggregates.

surfactant solution of 1.2% nanotube weight showed a final loading of 8.5% weight of nanotubes in the polymer. Thus, it is safe to assume that a lower percentage of nanotubes in the surfactant solution will produce lower loadings in the polymer. A good indication of the high level of interaction of the polymer chains with the nanotubes is that the complete dissolution of SWNT-PS specimens in an organic solvent (toluene) forms a homogeneous dark dispersion for a period longer than three weeks. Figure 1 (top) shows a photomicrograph of samples dissolved in toluene. Each sample contains approximately the same amount of SWNTs. The solution, made simply by dissolving polystyrene in toluene and then adding the tubes (left vial), had a very dark appearance after sonication for 2 h, but after 2 days black sediment and a clear solution separated. The vial on the right corresponds to SWNT-PS (8.5% loading) dissolved in toluene after more than three weeks.

Nanotubes alone are insoluble in all known solvents,⁵ therefore to form a stable mixture, as the one found in the current work, each nanotube must be sterically stabilized by attached polymer chains that impede flocculation and depletion aggregation phenomena. Solvent-cast films prepared right after sonication with these same polymer–nanotube solutions also presented a completely different microstructure under transmitted light microscopy (Figure 1, bottom), which is consistent with the attainment of higher dispersion of the inorganic reinforcement by the miniemulsion process.

The nanotube-filled styrene–isoprene (SWNT-SI) miniemulsion containing 0.6% weight of nanotubes was similar in color to the gray-bluish reacted polystyrene (SWNT-PS) miniemulsion. However, the bigger clumps of the modified elastomer aggregated more easily following precipitation into a somewhat elastic whitish rubber. This solid piece changed its appearance into an intense black after immersed for five minutes in boiling water. The coloration was uniform over the entire specimen. Once washed and set overnight in the

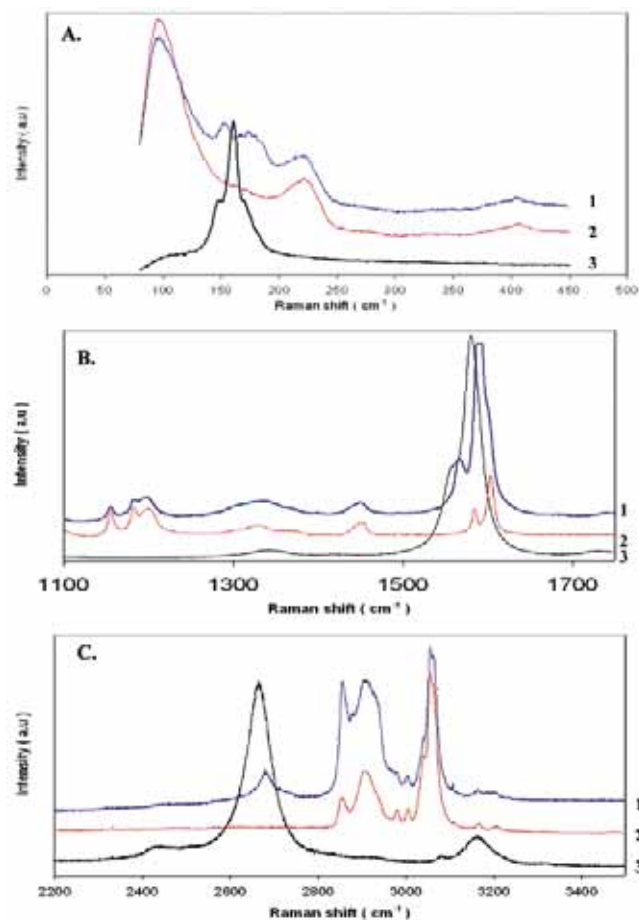


Figure 2. Raman spectra for SWNT-PS (1), Polystyrene (2), and Carboxylic SWNTs (3).

vacuum oven at high temperature (75 $^{\circ}$ C), no changes in coloration were detected. SWNT-SI was also completely soluble in toluene and THF for more than three weeks, which reinforces the idea of good polymer–nanotube interactions. The pure copolymer also has a rubbery consistency, but instead of turning black it becomes transparent after similar washes in boiling water followed by vacuum-oven drying.

Spectroscopy Results. Raman spectroscopy has been long recognized to be a powerful technique to probe the structure of polymers, especially those polymeric chains containing carbon–carbon double bonds. The same high resolution and versatility makes Raman analysis particularly important to study morphological and compositional parameters in SWNTs such as metallic characteristics, diameter, and presence of defects. In Figure 2a–c, three different frequency regions of the control-polystyrene spectrum are compared to that of the SWNT-PS composite for an excitation wavelength of 514 nm. By way of example, the spectrum of the nanotube powder is also shown. At very low frequencies (Figure 2a) the unmodified polymer shows a shoulder at 87 cm^{-1} and a broad peak centered around 220 cm^{-1} . The first shoulder has been assigned in the literature to the benzene group twisting in the polymer chain, while the broader peak has been related to the tangential C–H bending mode.¹⁵ It is interesting to note that no detectable changes in peaks location are apparent in the polymer as a result of the

insertion of the nanotubes. In contrast, the breathing mode for the SWNTs shifts to lower frequencies while the initial sharp peak centered at 160 cm^{-1} splits into two broader peaks of lower intensity. Theoretical¹⁶ and experimental work¹⁷ have shown that the radial-breathing mode (RBM) of SWNTs is largely affected by the surroundings of the individual tube. For instance, molecular simulations of the interfacial characteristics of a carbon nanotube–polystyrene composite system have demonstrated that the outer diameters of the single-wall and double-wall carbon nanotubes are reduced by about 0.6% as a consequence of the physical constraint introduced by the surrounding polymer chains. This radial deformation is believed to contribute to a great extent to the local mechanical interlocking mechanism for single-wall or double-wall carbon nanotubes; although it may not be as significant for multiwall tubes because of their better resistance to radial deformation. The broadened and somewhat split RBM region shown in Figure 2a for the SWNT-PS composite prepared by miniemulsion polymerization contrasts with the sharp peak obtained for the bare Carboxyl nanotubes. This in fact suggests that embedding SWNTs in a matrix results in a stiffening of the RBM, a physical phenomenon that was described by Buisson et al.¹⁷ as the equivalent to the classical modification of the eigenfrequency of a vibrating cord when immersed in water.

Figure 2b corresponds to the intermediate frequencies region. Herein, the spectrum of polystyrene is dominated by two main peaks at 1584 and 1603 cm^{-1} generally assigned to the tangential stretch mode of carbon–carbon bonds in the benzene ring. On the other hand, the so-called G-line feature centered at 1580 cm^{-1} dominates the nanotube spectrum. In the composites, the introduction of SWNTs causes a shift of the G-line to higher frequencies as well as a clear predominance of the 1590 cm^{-1} band. Similar results have been observed recently for nanotube-conjugated polymer composites, and it has been suggested that these changes may not be solely explained by a simple superposition of modes.⁵ For these authors, this phenomenon indicates an alteration of the vibrational structure of the polymer due to binding with the SWNT lattice. Finally, at higher frequencies (Figure 2c) the polystyrene spectrum has two distinct peaks of appreciably large intensities around 2915 and 3058 cm^{-1} . The former band is identified in polystyrene as originated by C–H chain vibration (C–H stretch mode), while the second major peak is related to C–H radial stretch in the benzene ring. Note that no significant changes operate in the composite spectrum in the high-frequency region after the introduction of the nanotubes.

In general, the same changes within the vibrational structure of the SWNT-PS can be found for the SWNT-SI. Mostly these changes manifested in the C–C stretch region as a strong shifting toward a predominant peak located at the 1590 cm^{-1} band. In addition, the characteristic vinyl or C=C stretching occurring as a very strong peak in the unmodified styrene–isoprene at 1670 cm^{-1} band dramatically loses its intensity as a result of the carbon nanotube incorporation. This constitutes evidence supporting the

Table 1: DC Electrical Resistivity Data at Room Temperature (12% RH)

polymer	thickness (cm)	SWNT loading (%)	ρ ($\Omega\text{-cm}$)
PS	0.059	0	$>2 \times 10^{16}$
SWNT-PS	0.073	3.5–4	$>2 \times 10^{16}$
	0.046	8.5	7.47×10^6

hypothesis of conformational changes in the polymer originating from interaction with the nanotubes.

Electrical Properties. Modification of the electrical properties of polystyrene and other polymers by introduction of inorganic reinforcements (e.g., carbon black, iron powder, etc.) has been long pursued by researchers.¹⁸ Recently, the use of MWNTs has been demonstrated as more advantageous than carbon black, not only because of the need of smaller loads to reach the conductivity threshold but also because their high aspect ratio helps create extensive networks that facilitate electron transport. SWNTs have not been studied as much as MWNTs in applications involving conductive nanotube-filled polymers. One reason for this is that strong attractive van der Waals forces lead them to aggregate easily, and thus, with the current solution cast techniques, it is very difficult to form conductive networks at relatively low loadings. Using the miniemulsion polymerization technique we have found that SWNTs can effectively disperse inside the host matrix and form multiple tube–tube contacts modifying the electric response of the composite. Table 1 summarizes the data corresponding to DC electrical resistivity measurements for SWNT-PS composites at three different loadings. These results are suggestive of a typical percolation system wherein the electrical properties of the composite would not be changed from those of the bulk polymer until the average distance between the nanotubes is reduced, such that either electron tunneling through the polymer or physical contacts may be formed. At the highest nanotube loading tried (8.5%) the SWNT-PS composite shows a dramatically lower volume resistivity than that of the pure polystyrene; but even so, this resistivity value is still high in comparison with composites made with low nanotube loadings in epoxy resins.¹⁹ The origin of such smaller conductive capacity of the nanotube network can be attributed to the internal resistance of an adsorbed layer of polymer that reduces the number of electrical contacts.² In fact, TEM micrographs of SWNT-PS material dissolved in toluene showed evidence that a layer of polymer was adsorbed on the nanotube bundles (Figure 3a). By way of comparison, a micrograph of bare Carboxyl (batch CLAP 8256) single-walled nanotubes is presented in Figure 3b.

Figure 4 shows a log–log plot of the impedance modulus, $|Z|$, with respect to frequency for different SWNT-PS (8.5% loading) disk-shaped molded specimens as well as two other reference materials: a typical insulator (polystyrene) and a semiconductor (silicon wafer, 0.98 mm thick). It is evident from these results that none of the nanotube composites display the ideal dielectric behavior exhibited by the pure polystyrene, and, in contrast, the samples range from pure semiconductor to clear ohmic behavior as the sample

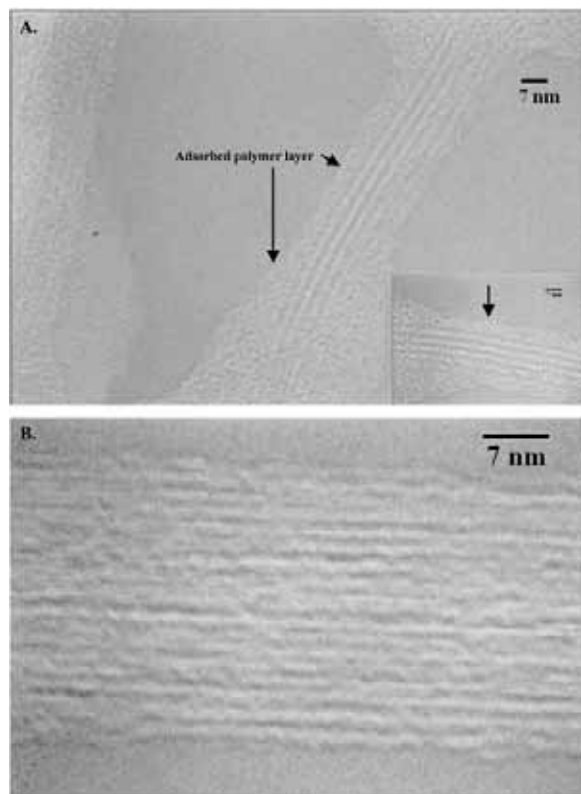


Figure 3. TEM micrographs showing (A) SWNT bundles with an adsorbed polystyrene layer in a 8.5% weight SWNT-PS composite and (B) bare Carbolex SWNTs bundles.

thickness decreases. For very thin samples (0.0276 cm) the frequency independence of the impedance modulus is sug-

gestive of an ohmic material that must possess a very well connected 3D nanotube network. As the sample thickness increases it appears that geometry starts playing a more significant role, making it difficult for the nanotubes to arrange themselves into an interconnected 3D net. The apparent invariance of the impedance modulus with respect to sample thickness, as well as the transition toward a semiconductor behavior, can be explained by considering the electrical conductivity to occur as a result of nanotube connections present only at the surface.

Conclusions. In this paper the possibility of utilizing a modified version of the miniemulsion polymerization technique to prepare SWNT-filled thermoplastic and elastomeric composites is demonstrated. Stable miniemulsions were formed by emulsifying a hydrophobic monomer under high shear (ultrasonication) conditions with the aid of a cationic surfactant (CTAB) together with purified carbon nanotubes. Polymerization inside the microdroplets was readily achieved by a combination of acid-catalyst seeding and oil soluble initiator at relatively mild temperatures. The incorporation of the nanotubes inside the polymeric matrix brought about physical changes such as a strong black coloration, as well as a substantial drop in the electrical resistivity from values greater than $10^{16} \Omega\text{-cm}$ for the unmodified polymer down to $10^6 \Omega\text{-cm}$ in the SWNT-PS composites with 8.5% nanotube loading. Raman spectroscopic analyses suggest that strong interactions between the nanotubes and the polymer chains take place, resulting in much less vibrational freedom of the polymer. Work in progress will attempt to perfect the polymerization method by controlling parameters such as surfactant load, hydrophobe/monomer ratio, type of initiator,

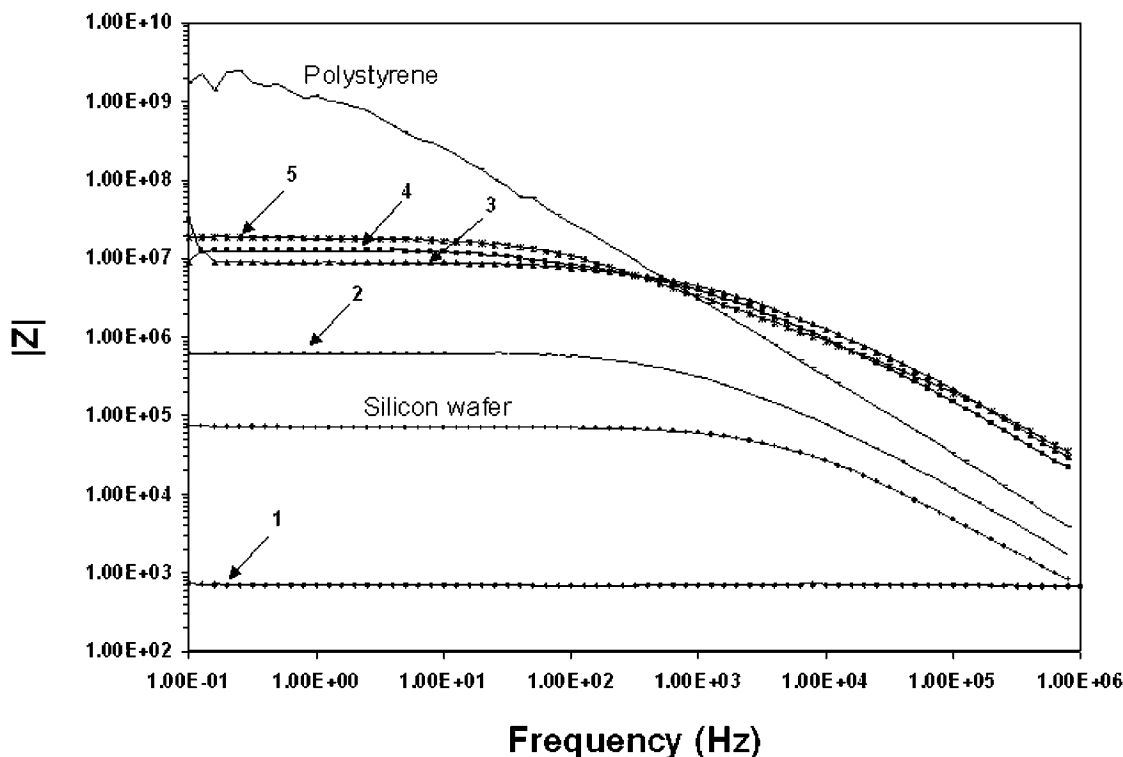


Figure 4. Log-log plot of the impedance modulus for 8.5% weight SWNT-PS composites of different thicknesses: (1) 0.0276 cm; (2) 0.0462 cm; (3) 0.0857 cm; (4) 0.1891 cm; (5) 0.2205 cm.

etc. Equally important will be to characterize both the SWNT-PS and SWNT-SI by electron microscopy (SEM, TEM) and dynamic mechanical analysis (DMA).

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