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Silanization of Carbon Nanotubes: Surface Modification and Polymer Nanocomposites

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1. Introduction

Since the first publication of successful silanization in carbon nanotubes (Velasco-Santos 2002) different research groups have opted for modify carbon nanotubes using various organosilanes. Silanization offer to carbon nanotubes (CNTs) the possibility to diversify their surface features depending on the organic part in organosilane inserted to nanotube surface. Silanized nanotubes show different features related with the silane used in functionalization. Dispersion of CNTs in organic solvents is modified by the organosilane type applied in silanization of nanotubes.

Silanization have been achieved in CNTs taking advantage of the carboxyl and hydroxyl groups produced during the oxidation process of nanotubes. Also, silylation achieved without previous oxidation and by hydroxylation have been developed. In addition, silanized CNTs (s-CNTs) are used to attach to nanotube surface other nanoparticles and molecules. This later is useful to create alternatives to functionalize or accomplish CNTs to other inorganic or organic nanometric structures. Due to the alternatives that the silanization offer to carbon materials, recently the successful approaches used to silanize CNTs have been applied to other carbon materials such as nanofibers and graphene.

In spite of silanization is a successful method to change nanotube surface behavior, to attach other molecules or chains to nanotubes, or linking CNTs with other nanostructures; this route with organosilanes is an established approach in polymer composites. In this type of chemical functionalization, silanes are used as coupling agents of glass and carbon fiber with polymer matrices in order to improve interface. In this context, silanization in CNTs, also have been proposed as nanometric coupling agent (Velasco-Santos 2002) of CNTs with polymer matrices and thus, recently silanized carbon nanotubes have been incorporated to develop polymer nanocomposites.

Thus, in the first part of this chapter are described the principles of silanization reaction achieved in CNTs and the characterization obtained in the first report. The second part of the chapter describes diverse researches of silanization reactions achieved in nanotube

surface, including silanization after oxidation, silylation and hydroxylation. Arrangement of some nanostructures attached to CNTs surface via silanization and functionalization of other carbon nanomaterials with organosilanes are also reviewed and discussed in this section. Finally, advances related with silanized carbon nanotubes as reinforced in polymer nanocomposites are analyzed. Hence, silanization is shown as important chemical route in order to attach different organic moieties, diversify carbon nanotube properties, develop new nanoarrangements and improve compatibility between CNTs and polymer matrices.

2. Principles of silanization in CNTs

As it was mentioned, carbon nanotubes exhibit amazing mechanical properties, such as exceptionally high Young's modulus, stiffness and flexibility (Lourie et al 1998; Yu et al 2000). Also the CNTs density is very low and their sp^2 carbon-carbon bond in the plane of the graphene lattice is among the strongest of all chemical bonds (Jin et al. 2001; Velasco-Santos et al. 2003). Therefore, one of the most proposed possible uses to CNTs is their incorporation to other materials with the aim to produce engineering composite materials in order to truly take advantage of their outstanding mechanical properties. Related with this, the functionalization has taken part in order to employ these materials as effective reinforcements in advanced composites, inasmuch as a good chemical bond to the matrix must exist, to effectively transfer mechanical loads from the matrix to the nanotubes and thus take advantage of their mechanical features. Accordingly, the addition of diverse chemical groups to the surface of functionalized CNTs has been proposed extensively (Velasco-Santos et al. 2004, Tasis et al. 2006, Karousis et al. 2010;) with the target to reach the compatibility between polymer matrix and CNTs and diversify their inclusion with different matrices. In this context the functionalization of CNTs with organosilanes inserted to oxidized Multiwalled Carbon Nanotubes (f-MWNTs) was proposed (Velasco-Santos 2002). Silanization provide a single approach in order to add different organic molecules to CNTs surface and in this way not only diversifying their surface behavior of these nanomaterials, but incorporate to nanotubes, a variety of chemical moieties depending on the coupled organosilanes; and thus open the opportunities to the silane function as coupling agent of different organic compounds, polymer matrices, nanomaterials and nanostructures. Principles and details of silanization reaction on CNTs and characterization of these materials are described next.

Organofunctional silanes coupling agents have been attached to CNTs follow diverse approaches. However, the first silanization on CNTs reported took as base the typical silanization reaction achieved in different fibers such as: glass, carbon and naturals. Organosilanes are substances that allow us to chemically join two materials. This "link" can be accomplished through chemical bonds or physical interactions. The organosilanes are chemically described as:

$$R\text{-}Si\text{-}R'_3$$
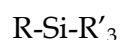
where R is an organo-functional group attached to silicon. In the silanization on CNTs have been proposed that the R group can be chosen to be reactive depending on the organic matrix being used. Silane also could be selected depending on the nature of the material to be attached to CNTs surface. In the other hand the R' group reacts through silicon-oxygen fiber bonds and is generally trimethoxy $3(OCH_3)$ which is easily hydrolyzed to form a trisilanol. This group reacts readily with the hydroxyl groups (produced through oxidation)

on the nanotube surface. The sequence is schematically shown in Figure 1, where the chemical structure of the organosilane is again represented (Figure 1a), along with the reaction scheme (Figure 1b) and a representation of silane chemical interactions on the nanotube surface (Figure 1c). Also, in this scheme are represented two R groups as R1 and R2 with two different organosilane moieties that have been attached to functionalized CNTs (f-CNTs) with the same approach; 3-mercaptopropyl trimethoxysilane (3-MPT) and 3-methacryloxypropyl-trimethoxysilane (3-MAT). As it was mentioned, silanization have allowed adding new chains to the open end cap and to the walls of the MWNTs oxidized before, aiming to improve their compatibility to polymer chains. Besides, the method is useful to link CNTs with other chemical groups depending on R terminal group.
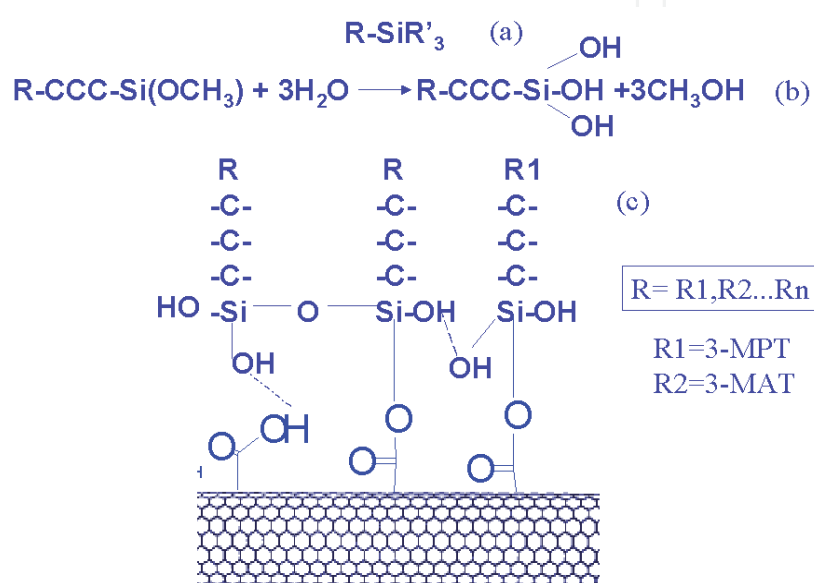

Fig. 1. Sequence of silanization reactions on nanotubes surfaces.

As it was mentioned before, oxidation is the first step in some researches focus to subsequent silanization of CNTs. Nowadays there are several methods in order to oxidize the CNTs surface (Velasco-Santos et al. 2004, Wiltshire et al 2004, Datsyuk et al. 2008). For the first silanization on CNTs the method to achieve the oxidation of CNTs involves $KMnO_4$ as oxidant in acid media. In this report MWNTs obtained by the arc-discharge method were employed. Oxidation was developed according to the report of Hiura 1995, but with slight variations in the quantity of $KMnO_4$ and reflux time. The chemical nature of the purification and functionalization of CNTs is due to the other carbon forms presents are oxidized almost completely, and new groups are produced on the tube surface, mainly in the nanotubes tips, which in turn increases the reactivity and allows us to attach either organic and inorganic moieties as has been done in other carbonaceous materials.

After the oxidation, funtionalized Multiwalled Carbon Nanotubes (f-MWNTs) were reacted with the organofunctional silane 3-mercaptopropyl trimethoxysilane (3-MPT) and 3-methacryl trimethoxysilane (3-MAT), in both cases the reaction was performed with 25 mg of f-MWNT; the silanes were used in liquid form, and were diluted in ethanol prior to the reaction, in order to make an alcoholic solution. In these solutions f-MWNTs were added slowly to ensure an even distribution. The amount of used organosilane was 1:1 in weight with respect to the f-MWNTs. The mixes were refluxed for 3 h, maintaining the temperature

around 65-70°C and under constant stirring. The silanized functionalized multiwalled carbon nanotubes (identified as fs-MWNT) were dried at 100°C for around 12 h to allow a complete evaporation of ethanol, followed by washing with hot water and acetone to eliminate any non-reacted organosilane.

Figures 2a and 2b show a comparison between MWNT and f-MWNT FTIR spectra. The bands in both spectra at 840 and 1587 cm^{-1} are due to the A_2u and E_1u IR phonon modes present in carbon nanotubes (Kastnert 1994, Saito 1998); the f-MWNTs were terminated with carboxylic acid groups and carboxylate. This is seen in low intensities of the band around 1740 cm^{-1} which correspond to v(C=O) typical of carboxyl moieties. Other evidence of carboxyl group is a slight increase in 1346 cm^{-1} δ(O-H) in plane and 960 cm^{-1} δ(O-H) out of plane bands (Coates 2000). Also, a higher intensity is seen in the band around 1495 cm^{-1} and in the peaks between 1600 cm^{-1} and 1680 cm^{-1} in comparison with the zone above 1700 cm^{-1}, these corroborate that quinone and carboxylate groups exist in these oxidized nanotubes (Coates 2000, Zhang 2003, Chen 2001, Ma 2006). The peak at 1576 cm^{-1}, assigned to -C=C in spectrum a), is notably weaker than that in spectrum b); this indicates changes in CNTs surface due to oxidation (Zhang 2003) , inasmuch as, it is known that some damage is produced in CNTs walls. In figure 2c) are found results of successful silanization process; the bands at 794 cm^{-1} and 919 cm^{-1} are typical for v(Si-OH) and δ(OH) out of plane. These bands appear when trimethoxy groups are broken in order to form silanol groups. The silanol groups provide interactions between oxygen of carboxylates and hydroxyl moieties of oxidized nanotubes and the organosilane. In addition spectrum 2c) does not show bands between 815 cm^{-1} and 845 cm^{-1}, characteristic signals of nonreacted SiOR groups in organosilane compound (Velasco-Santos 2002, Bourgeat-Lami 2002). The bands at 1045 cm^{-1} and 1111 cm^{-1} are due to Si-O-Si and Si-O-C vibrations (Bourgeat-Lami 2002, Coates 2000) and correspond to siloxane units formed during silanization process. The high intensity band at 1740 cm^{-1} becomes stronger due to the ester group v(C=O) vibration which corresponds to methacrylate moiety in this case of the organosilane attached to CNTs.
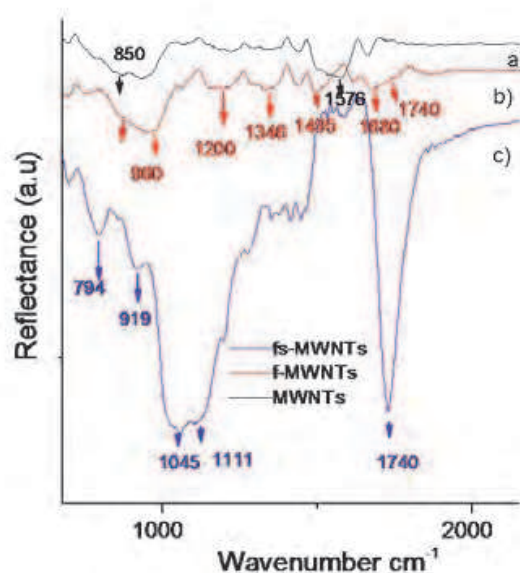

Fig. 2. Infrared Spectra of a) MWNTs, b) f-MWNTs, c) fs-MWNTs (3-MAT).

Figures 3a and 3b show the MWNT and f-MWNT Raman spectra. In both cases, two bands at 1576 cm^{-1} (G line) and 1328 cm^{-1} (D line) appear. The first peak corresponds to the E$_{2g}$ modes, which has been assigned to the movement of two neighboring carbon atoms in opposite directions, characteristic of highly oriented pyrolitic graphite (HOPG). The second signal is due to the disorder present in the MWNTs, a feature related to the region near the K-point phonon of the graphite´s Brillouin zone (Zhao 1998, Wang 2002, Dresselhaus 2002). It is clear that in this case the ratio of intensities between D and G peaks changes in the f-MWNT spectrum (figure 3b) with respect to the MWNT spectrum (figure 3a), this is due to the formation of sp^3 hybridized carbon "defect" sites on the carbon nanotubes walls due to the addition of the functional groups (COOH), which supports the results obtained in the FTIR analysis. The Raman spectrum of fs-MWNTs is shown in figure 3c, where no changes with respect to the f-MWNT RAMAN spectrum are observed in this case; since the bands in this spectrum represent details of the carbon nanotubes crystalline structure, in which silanization does not take place. The changes are observed when the functionalization is performed through oxidation directly in the end cap and sidewall carbon nanotubes due to the insertion of carboxylic groups such as it have been indicated before. Also, silanization analysis are completed in this research by elemental analysis obtained by Energy Dispersion Spectroscopy (EDS); in this case of CNTs silanized with 3-MPT. A clear 12% of Si is obtained to fs-MWNTs.
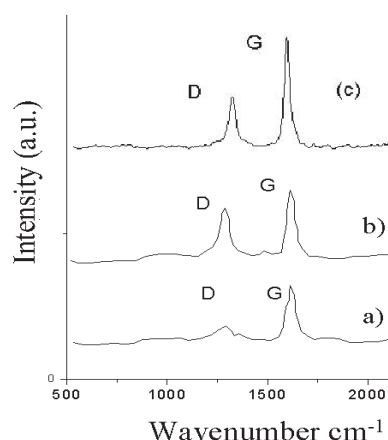

Fig. 3. a) Raman spectra of a) MWNTs b) f-MWNTs, c) fs-MWNTs.

The oxidation and silanization in CNTs yields functionalized moieties, which contain R groups bonded to the nanotubes by silanol groups. Thus the approach in this research allows modifying oxidized nanotubes with many different materials chemically-bonding to f-MWNTs in this case, inasmuch as the R group (methacryl, glycidoxy, etc) in the organofunctional silanes have been changed in different researches depending on the specific polymeric matrix employed for a particular use. The behavior of fs-MWNTs changes when the R terminal changes also, consequently it have found that fs-MWNTs (3-MAT silanization) produce soluble MWNTs (s-MWNTs) in organic solvent such as acetone or ethanol (Velasco-Santos 2004), inasmuch as the methacryl chain attached as R group in the fs-MWNTs surface changes the character of this material which allow their solubility, this does not occur when 3-MPT is attached in fs-MWNT due to the thiol group produces different properties in f-MWNTs surface. The figure 4 shows three kinds of CNTs: MWNTs, f-MWNT and fs-MWNTs (3-MAT), the samples were dissolved in acetone by 5 minutes in

ultrasonic bath in order to disperse the CNTs, then, the samples were kept on repose 5 minutes. The image shows that the sample "c" which correspond to fs-MWNTs (3MAT) presents the most black color intensity due to these fs-MWNTs stay disperse more time in the solution in comparation with MWNTs and f-MWNTs which stay disperse by some minutes and after precipitate. The fs-MNWTs stays in solution during days forming a homogeneous solution.
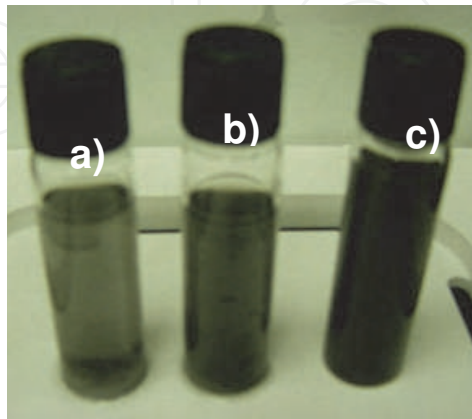

Fig. 4. Samples of carbon nanotubes dissolving in acetone, a) Multiwalled carbon nanotubes (MWNTs) , b) oxidized functionalized multiwalled carbon nanotubes (f-MWNTs), c) silanized functionalized multiwalled carbon nanotubes (fs-MWNTs). (Velasco-Santos 2003).

3. Silanization of carbon nanotubes

Once that silanization was reported as single and efficient approach in order to modified CNTs with several organic molecules, different researches have been focus to attach diverse organosilanes. Next are reviewed the silanization routes employed and the silanes linked to nanotube surface.

Bag et al. 2004, silanized CNTs also with 3-MAT. In this research the previous oxidation is achieved by $KMnO_4$ as oxidant along with a phase transfer catalyst (Aliquat-336 in acetic acid media). Authors mention clearly that the aim of silanization is as well to get a modified CNTs linked with the coupling agent having a functional group such as a double bond which can be utilized further for copolymerization with other vinyl monomers and also improve interface of CNTs with polymer matrices. For the silanization 0.024 g of oxidized CNTs are mixed by sonication for 15 min with 2 ml of 3-MAT in toluene solution. Reaction is achieved at 100 ◦C for 6 h with stirring .The product is washing with deionized water and acetone. The resulting material (fs-MWNTs) was separated by a centrifugation and drying in a vacuum oven at 80◦C.

Silanization is confirmed in this research by IR spectroscopy and EDS. Results show similar evidence that those found by previous reports of silanization on CNTs (Velasco-Santos 2002, 2003). IR signals in 1090 cm^{-1} due to Si–O vibration, at 798 and 960 cm^{-1} due to Si–OH and other bands related with alkyl chains to the organosilanes corroborate successful silanization. Also, the quantity of Si measure by EDS in fs-MWNTs completes the information.

Vast et al 2004 modified MWNTs using ((tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane) (FTCS). In this research carboxyl and hydroxyl groups of the previously oxidized MWNTs

are taking in advance in order to link the silane to CNTs surface. For the oxidation of CNTs in this research is used a acids mixture. 5 g of MWNTs are dispersed in a solution of 400 ml of H2SO4/HNO3 (3:1 v:v) at 50 ◦C and stirred for 20 h. However in this research the carboxyl groups produced during oxidation process are also reduced. Both systems; Oxidized CNTs and reduced CNTs after oxidation are silanized. For the reduction of the carboxylic acid of CNTs; 0.6 g of oxidized nanotubes are dispersed in dry tetrahydrofuran (THF) at 0 ◦C, under argon atmosphere. 14 ml of diisobutylaluminium hydride (DIBAL-H) are added and the solution is stirred for 3 h at room temperature. The solution is filtered, washed with dry THF and reprotonated by stirring the nanotubes with ethyl alcohol. Solvent is eliminated by filtration and the powder is dried at 60 ◦C for 12 h. For the silanization of both materials (oxidized MWNTs and reduced MWNTs); 0.2 g of activated nanotubes are dispersed in 40 ml of dry toluene by ultrasonic head under argon atmosphere. Then 0.25 g of triethylamine are added and stirring in order to deprotonate carboxylic acid or alcohol groups. 25 ml of a 10^{-2} M toluene solution of FTCS are added to the nanotube mixture and stirred for 20 h. The filtration of nanotubes is followed by three successive sonications in toluene to eliminate unreacted silane. Finally, the powder is dried in an oven at 90 ◦C for 20 h.

The silanized nanotubes obtained by this process show different bonds related with those found in the previously silanization. The links between CNTs and FTCS are corroborated by X-Ray electron spectroscopy (XPS) and shown that both kinds of CNTs are successfully silanized. The covalent bonds that prevail in both silanization are $Si-O-C_{NTS}$ and Si-O-Si. Thermogravimetric Analysis (TGA) of both kinds of silanized CNTs and the analysis of the residual mass by XPS shown a slight appear of Si-O bonds in the reduced CNTs. However the authors mention that reduction after oxidation does not induce major differences on the silanization level on CNTs.

Ma et al. 2006 silanized CNTs with 3-glycidoxypropyltrimethoxy (3-GPTMS), also using oxidized CNTs. The oxidation method employed in this research involves UV/O_3 treatment in a chamber and reduction of carboxyl groups on CNTs as was proposed by Vast el al 2004. However the approach used to reduction of oxidized CNTs is different to the reported for Vast et al. The reduction of the oxidized MWNTs is realized using lithium aluminum hydride (LiAlH4). 20.0 mg of f-MWNTs are dispersed in toluene by ultrasonication for 30 min. Then 5.0 mg of LiAlH4 are added. The solution is stirred for 1 h at room temperature. Next 2.0 ml of 2.0 N hydrochloric acid are added into the solution in order to remove the lithium and aluminum. The reduced MWNTs are obtained after filtration of the solution and washing with toluene, absolute ethanol and acetone and drying in a vacuum oven at 80 ◦C overnight.

For Silanization 20.0 mg of reduced MWNTs with 50.0 ml toluene are sonicated for 30 min. Then 7.5 ml of 1.0 wt% toluene solution of GPTMS are added and stirred for 6 h at 60–65 ◦C. After the reaction, 30 ml of methanol are added to dilute the unreacted GPTMS. The fs-MWNTs are obtained by filtration and washing with methanol, water and acetone sequentially. fs-MWNTs are dried in a vacuum oven at 80 ◦C for 12 h.

fs-MWNTs are characterized by IR, EDS and Transmission Electron Microscopy (TEM). Infrared analysis of nanotubes shown typical bands after oxidation related with COOH which are converted to OH after reduction. After silanization the analysis of IR spectrum only is focus to the bands related with epoxy alkyl groups of GPTMS. XPS show similar bonds in fs-MWNTs that those found by Vast et al. $Si-O-C_{NTs}$ and Si-O-Si are found by this

technique. Also, the possibility of the damage to the MWNT surface after silanization is studied by TEM. Fs-MWNTs are heated at 400 °C in atmosphere of nitrogen for 1 h in order to remove silane groups and observe the structure of these materials after silanization. TEM image of this process is shown in the figure 5. This micrograph suggests that the silane molecules on the MWNT surface can be removed, zone A and B in Fig. 5 shown typical damages after light oxidation but there are not extra damage in the walls. The layered structure of the MWNTs remained largely intact during the silanization process. These results are agreed with the Raman analysis reported by Velasco-Santos et al 2002. Raman spectra of f-MWNTs and fs-MWNTs are practically similar showing not extra damage after silanization.
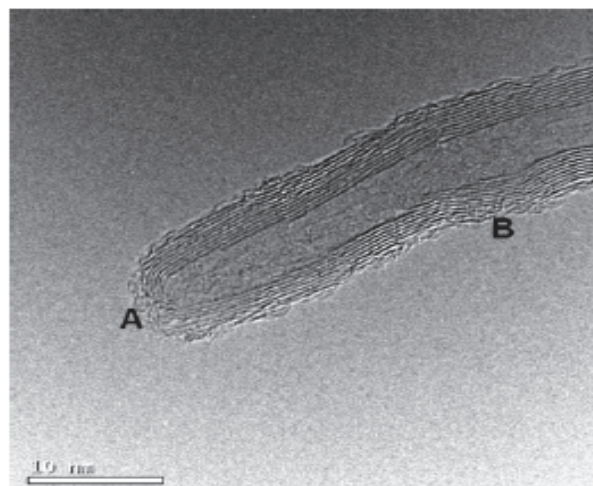

Fig. 5. Surface of fs-MWNTs, after decomposition of organosilanes. Copyright Elsevier Science

Recently, other researches have followed the tendency of attaching organosilanes to carbon nanotubes via carboxyl and hydroxyl groups produced during oxidation. With the same propose of improve interface of CNTs with different organic polymer matrices, amino silanes have been incorporated to MWNTs after oxidation. Kathi and Ree 2008, Scheibe et al 2009, silanized CNTs with 3-aminopropyltriethoxysilane (3-APTS). In the first research oxidation of MWNTs is achieved with acids mixture using H2SO4/HNO3 (3:2 v/v) at 50 °C and stirred for 20 h. For silanization .050 g of f-MWNTs are dispersed in 50 ml of ethanol via ultrasonication for 30 min. Silanization is realized with 3-APTS at 70 °C for 4 h and stirring. The fs-MWNTs are washing with water and acetone. Fs-MWNTs are separated by filtration and dried under vacuum at 80 °C for 12 h.

fs-MWNTs produced by Kathi and Ree are characterized by IR, EDS, TEM and Scanning Electron Microscopy (SEM). Microscopy images of silanized CNTs in this investigation allow concluding to authors that some amorphous material is deposited in tip and walls of these carbon materials. Also weak bands of absorption are observed to 1,070 cm^{-1}, attributed to a Si–O vibration and 803 cm^{-1}, related with Si–OH. Elemental Analysis of fs-MWNTs shows a 2.34 atomic % of Si.

In the other research about silanization of CNTs with 3-APTS (Scheibe et al 2009), acid mixture of HNO3/H2SO4 (v/v = 1:3) at 175 °C for 18 h is used to oxidize MWNTs. The acidic solution with f-MWNTs is diluted with purified water obtained of reversed osmosis process (RO H2O) and filtrated through a polycarbonate filter. Then, the sample is washed

with RO H_2O and acetone. f-MWNTs are dried under vacuum conditions at 180 ∘C for 1 h in order to eliminate adsorbed CO_2 and H_2O.

Then, two kind of silanization are developed for f-MWNTs, the different of the processes is basically the solvent used to rinse and to disperse the f-CNTs (acetone or RO H_2O). This and other conditions in the process according with the solvent used, produce notable differences in the silanized CNTs. Before to the silanization process f-MWNTs are divided in two parts and dispersed in RO H_2O, under vacuum in ultra-sonication bath at 60 ∘C for 20 min. Then silanization is achieved for each sample. Next both processes used are described: For the first sample, f-MWNTs are filtrated through a polycarbonate filter and washing with acetone in order to eliminate adsorbed water molecules and this way avoid hydrolysis. Then, the obtained sample is re-dispersed in acetone in a test tube and placed onto the magnetic stirrer. Next APTS solution is added slowly to the dispersed f-MWNTs solution, until the silane concentration reaches the 2%., the mixture is stirred under vacuum conditions for 15 min. Next, the pressure is elevated until the atmospheric pressure and the mixture was left for 30 min at room temperature. The final product obtained in the experiment I is well dispersed solution.

For the second silanization process, the solution is filtrated through the polycarbonate filter and rinsed in this time with RO H_2O. The obtained sample is re-dispersed in RO H_2O in the test tube in the ultra-sonication bath under vacuum conditions at 40 ∘C for 20 min. Then, pH of f-MWNTs solution is adjusted to 4.0 with glacial acetic acid. Next, APTS solution is added slowly to the dispersed f-MWNTs solution, until the silane concentration reaches the 2%. Subsequently, the mixture is sonicated under vacuum for 15 min and after the sample reaches the atmospheric pressure. The mixture is left for 3 h in a closed tube at 40 ∘C. The final product obtained in the experiment II gives weakly solubility.

After each silanization procedure, the mixtures are filtered through a polycarbonate filter, and rinsed with acetone in order to remove excess of the aminosilane molecules and dried. The most outstanding results in this research are obtained by the techniques IR, TGA and HRTEM (High Resolution Transmission Electron Microscopy) for both kind of fs-CNTs and the samples used as comparison, such as purified MWNTs and f-MWNTs. Besides of corroborated oxidation by the typical bands in f-MWNTs; IR spectra of silanized CNTs show typical bands of successful silanization. The presence of weak signals at 1110 cm^{-1} related with Si-O-C and 875 cm^{-1} which correspond with Si-OH found also in other researches confirm silanization in both kinds of fs-MWNTs. However other weak signal is found at 1161 cm^{-1} only for the silanization achieved in the experiment II, and is related with Si-O-Si. Authors associate this band with the APTS hydrolysis and its self-condensation which occurred by the conditions employed in the experiment II. This fact is also link due to the aminosilane layer found in TEM fs-MWNTs (experiment II) is thicker than the layer of the fs-MWNTs (experiment I). In addition TGA confirm better thermal stability for CNTs silanized by the conditions of experiment II than CNTs silanized in the experiment I. Thus the second process is favorable in order to obtain thicker aminosilane layer and a system thermally more stable.

Hemraj-Benny and Wong 2006 functionalized CNTs with trimethoxysilane and hexaphenyldisilane. However their silylation protocol does not require previous oxidative methods. The study is focus to explore the photochemical silylation of SWNTs, taking in count an analogous reaction to that involving fullerenes. Authors assume that the reaction scheme of the silylation of SWNTs is similar to that of fullerenes due to the nature of both materials.

For the silylation of SWNTs adducts, they use two reference samples: purified SWMTs and control SWNTs. In order to prepare control SWNTs a sample of purified CNTs is placed in

2-propanol and stirring for 48 h with exposure to the UV lamp. Authors confirm by HRTEM and that there is not visible damage occurring on tube sidewalls. Before to the silylation, SWNTs are dissolved in the presence of dry 2-propanol and flushed continuously with argon. For the reaction with hexaphenyldisilane, 50 mg of the silane precursor are placed into a Schlenk flask with 20 ml of dry 2-propanol, this solution is combined with the SWNT dispersion. The mixture is irradiated with a 500 W mercury xenon lamp for 48 h. The functionalized adduct was isolated by filtering over a 0.2 μm polycarbonate membrane. Then sample is washed with 2-propanol and distilled water to eliminate unreacted silane. For the sylilation with trimethoxysilane, hydrogen hexachloroplatinate(IV) hexahydrate (38-40% Pt) is used as catalyst and represent the main difference with respect to hexaphenyldisilane reaction . In this case, the catalyst solution is initially added to a solution of SWNTs, and then 0.016 mol of the organosilane is incorporated. The process is performed under Schlenk conditions to ensure the absence of moisture. Sample is irradiated for 48 h and filtered and washed.

Results of both sylilation processes show important variations. Data obtained of AFM (Atomic Force Microscopy) for both samples indicate an average height of 6.99 ± 1.53 nm for the SWNTs adducts modified with trymethoxysilane and 7.03 ± 2.56 nm for the SWNTs adducts functionalized with hexaphenyldisilane. The average height for the SWNTs control adduct is 3.92 ± 1.58 nm. This indicates a coating produced in adducts due to the silane in the CNTs surface. Raman spectra analyses of both silanized samples are examined considerer two zones. The first zone is related with the signals D and G typical bands in carbon nanotubes. The intensity of these bands is related with the purity but also defects of CNTs and therefore some changes in the D/G ratio several times are related with structural modifications. In this case authors compare the values obtained by 1-D/G at different excitation wavelengths to verify structural changes; the results indicate similar trends found for all utilized laser. The expression values decreases upon chemical functionalization. The functionalized SWNTs show lower values of the expression 1-D/G than SWNTs and control SWNT. However, trimethoxysilane-SWNT adduct shows the smallest value of this expression. These results suggest a more effective sidewall functionalization of SWNTs with trimethoxysilane as compared with hexaphenyldisilane. Raman analyses are completed with the estimated atomic concentrations obtained by XPS; control SWNT adduct does not contain Si and the values obtained for trimethoxysilane-SWNTs and hexaphenyldisilane SWNTs are 7.99 and 1.55 respectively. The highest Si contain for the first sample also is related with effective functionalization and is agree with Raman results.

The second zone analyzed in Raman spectra is related with Radial Breathing Mode (RBM). This signal for CNTs is related with the nanotube diameter and some values of wavelength for this band have been assigned to metallic or semiconducting CNTs. The bands assigned to metallic nanotubes show more intensity for trimethoxysilane-SWNTs than the signals related with semiconducting behavior which decrease in intensity as compared with non modified SWNTs. The same signals (related with metallic and semiconducting tubes) show different behavior for the hexaphenyldisilane SWNTs, inasmuch as, signals related with both features decrease in intensity as compared with pristine SWNTs. Thus, authors conclude that trimethoxysilane has less reactivity with metallic nanotubes and this reaction has preferential selectivity for semiconducting CNTs. However, hexaphenyldisilane reaction is less selective to the diameter and the structural features of CNTs. This suggestion is also corroborated by UV-Visible-NIR spectroscopy; the absorption bands obtained by this technique which correspond with electronic transitions (metallic and semiconducting) are

presented in control SWNTs adducts. However, in adducts modified with hexaphenyldisilane the bands of all electronic transitions disappear indicating that sp^2 hybridized structure is changed. For trimethoxysilane-SWNT adducts prevail the absorption bands related with metallic features and semiconducting electronic transitions disappear. This confirms the reaction tendency of each silylation process.

IR analysis of these adducts corroborated that silylation is achieved by covalent bonds Si-O-C and Si-C, but silanol groups are not produced in the reaction. In the IR spectra the signals for adducts are compare with silane precursor. For trimethoxysilane-SWNT adduct, the bands related with Si-O-C stretching and bending are found at 1037 and 737 cm^{-1} respectively; these peaks are presented in the precursor at 1074 and 787 cm^{-1}. The shifts are related with the link between silane and CNTs. For the spectrum of hexaphenyldisilane SWNTs adduct the signals detected are related with the silane precursor attached to CNTs; bands of Si-C stretching vibration are found at 1257 and 1099 cm^{-1}. In both spectra of functionalized CNTs are not found signals at 798 and 956 cm^{-1} which are related with Si-OH groups. This corroborates that bonds between silane and CNTs are produced directly. A proposal of link in SWNTs surface for each silane is shown in the figure 6.

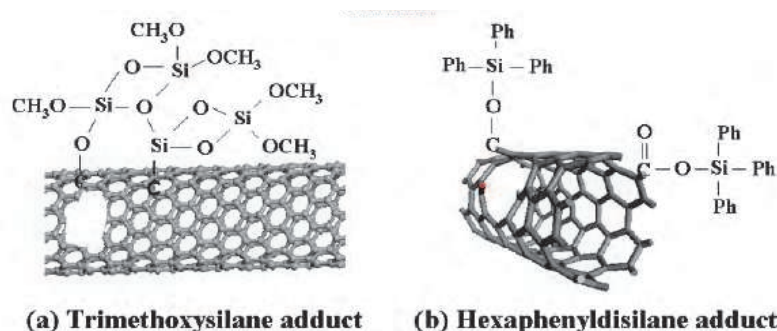(a) Trimethoxysilane adduct   (b) Hexaphenyldisilane adduct

Fig. 6. Schematic representation of SWNTs modified with silane precursors. Copyright ACS.

Lee et al 2009 develop silanization without previous oxidation using spontaneous hydrosilylation reaction that induces direct C–Si covalent bonds. They use triethylsilane (TES) due to the molecule contain a neutral Si–Hx moiety. Hydrosilylation is used in this research because of is efficient catalytic reaction useful for the insertion of silicon-based functional moieties into unsaturated hydrocarbons, such as alkenes or alkynes. Thus, the sp^2 hybridized structure could be modified in similar way. However the main purpose of authors is focus to use the hydrosilylation reaction in order to silencing metallic SWNTs from mixtures. The silencing of metallic SWNTs would allow fabrication of network-type SWNT field-effect transistor (FET) devices showing high on/off ratio.

The Hydrosilylation reaction is performed in an N2-filled glove bag. Diluted TES solutions are prepared in hexane at various concentrations. Substrates previously prepared containing SWNTs are immersed in TES solution for 1 h at room temperature. The sample are washed with hexane and isopropyl alcohol, and dried with N2.

Successfully hydrosilylation is corroborated by Raman analysis by the changes in D/G ratio of the band areas of SWNTs spectrum after reaction as compared SWNTs spectrum before reaction. Substantial increase of the D band and therefore changes in the values of D/G ratios are related with the breakdown of sp2 conjugations by hydrosilylation reaction. Authors also probe the silencing metallic by hydrosilylation verifying the changes in the current–gate voltage (I–Vg) curves of SWNT-FET (Field Effect Transistor) devices before and

after the hydrosilylation reaction. Results show dramatic increases in on/off ratio observed when the original devices react with 1mM and neat TES for 1 h. These results imply that the hydrosilylation reaction is indeed effective for silencing metallic SWNTs to give semiconducting nanotubes at wide ranges of silane concentration.

The two latter reviewed researches, give important evidence related with the silanization process is an important route not only to compatibilize molecules with CNTs; also, selective electronic behavior can be induced. Thus, silanization using previous oxidation or produced directly on CNTs surface is a versatile functionalization approach that opens different alternatives to diversify CNTs research and applications. Next are reviewed some silanization process in order to attached nanoparticles.

4. Nanoparticles attached on carbon nanotube via silanization

Recently silanization also have emerged as important route to diversify nanoarchitectures derived of CNTs. Lin et al 2009 use organosilane chemistry in order to attached magnetically iron oxide- in-silica nanoparticles and also polyethylene glycol to CNTs surface by similar protocols. Silanization is achieved taking advantage of the carboxyl and hydroxyl groups produced by oxidation; trimethylchlorosilane is used as coupling agent. Next is described the modification of silanized SWNTs with nanoparticles. For this propose a solution containing a dispersion of 3 mg of encapsulated magnetic iron oxide silica nanoparticles (prepared previously) and 1 ml of triethylamine is combined with 3 mg of the silanized SWNTs. The mixture is ultrasonicated for 15 min and stirred for 12 h. The resulting product is rinsed by benzene and distilled water, respectively, in order to remove the residual nanoparticles. Then fs-SWNT is filtered and dried at 60 ºC overnight. TEM images of the nanoparticles attached to CNTs are shown in the figure 7.
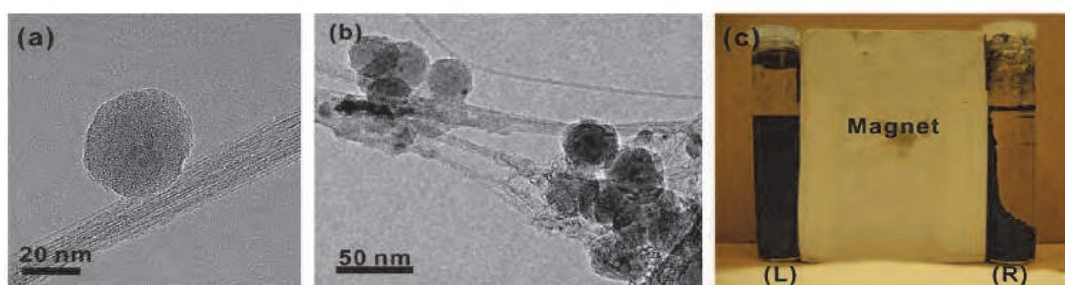

Fig. 7. TEM images of fs-SWNTs-(Fe$_3$O$_4$@SiO$_2$) nanoparticles; a) Interaction between nanoparticles and fs-SWNTs adduct, b) Different nanoparticles attached to fs-SWNTs adduct , c) Dispersion of (L) oxidized SWNTs mixed with Fe$_3$O$_4$@SiO$_2$ nanoparticles in ethanol exposure to a magnetic field, (R) fs-SWNTs-(Fe$_3$O$_4$@SiO$_2$) nanoparticles in ethanol exposure to a magnetic field. Copyright Elsevier Science.

Liu et al. 2008 as well modified CNTs with nanoparticles using silane as part of the coupling agents in their reaction procedures to develop nanoarchitectures based on MWNTs. They synthesize a silica–polymer–CNT hybrid. The nanotubes are encapsulated by poly(3-acrylaminopropylsiloxane) with silica nanospheres on the polymer surface. Reactions are sequence are next : 1) reactive poly(acryloyl chloride) (PAC) is grafted on the CNTs through the reaction of side acyl chloride groups taking advantage of the hydroxyl groups produced after oxidation. 2) 3-aminopropyltriethoxysilane (3-APTS) react with grafted PAC through

the reaction between amino and acyl chloride, siloxane-containing sub-grafts are introduced onto the primary PAC grafts. 3) silica nanospheres are covalently attached to the sub-grafts by condensation. The intermediate structures in this research are confirmed by authors by IR spectroscopy and XPS. Figure 8 shown the reactions sequence on CNTs surface including organosilane insertion. Figure 9 shown TEM images of silica nanoparticles and the hybrid nanostructures based on CNTs.
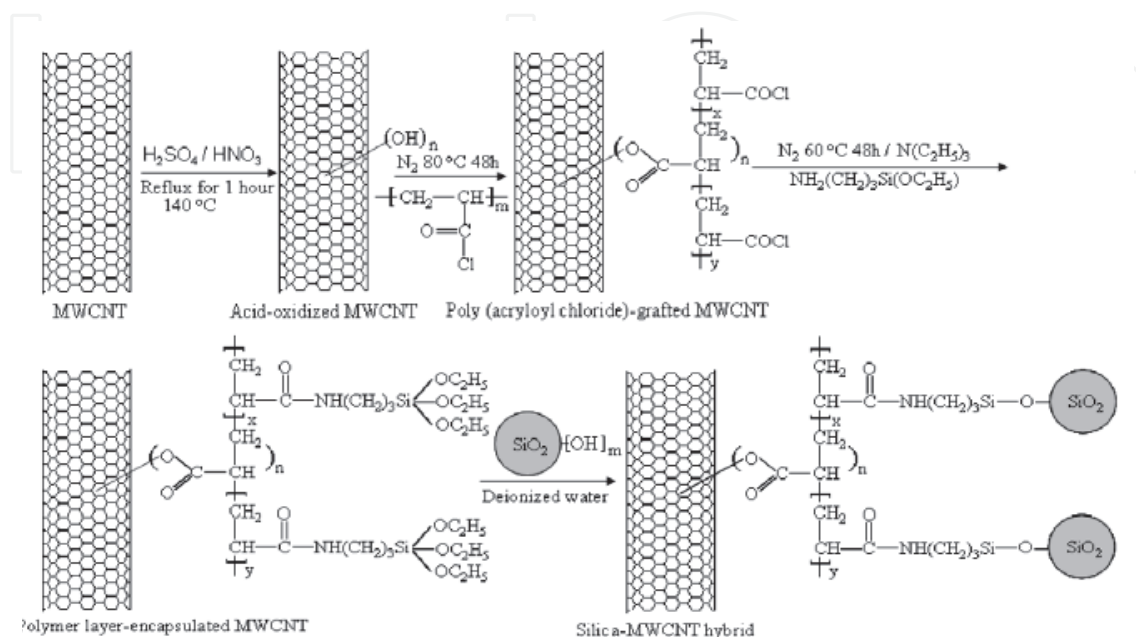

Fig. 8. Schematic representation of the reaction sequence to develop MWNT-polymer-silica nanoparticles hybrids. Copyright Elsevier Science.
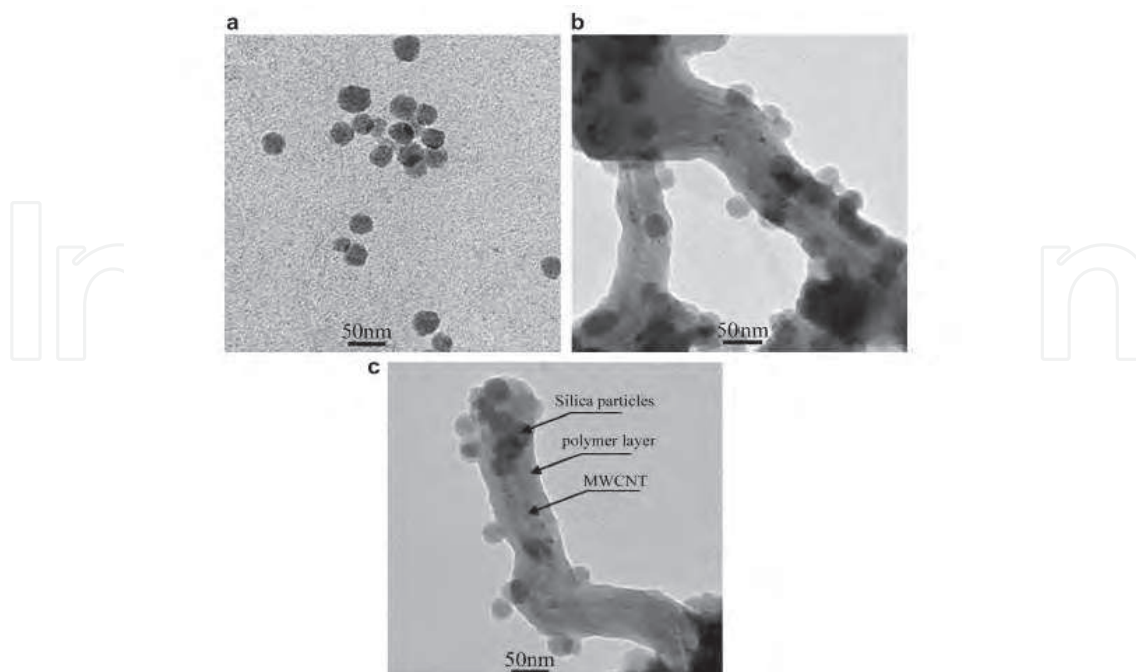
Fig. 9. TEM images; a) silica nanoparticles, b-c) MWNTs-polymer-silica nanoparticles hybrid. Copyright Elsevier Science.

5. Silanization of carbon nanomaterials

Due to the silanization is relatively a single reaction, and recently advances in research on CNTs have shown that is an effective method not only to insert organic chains such as been reached in microscopic fibers, but also to produce important progress in diversify CNTs properties and possible applications. Nowadays, some groups have used silanization in order to modify other carbon nanoforms. Carbon nanofibers (CNF) and graphene oxide (GO) are two carbon nanostructures modified by silanization effectively. Palencia et al, 2009, developed a complete study related with silanization conditions of CNF. Time, Temperature, silane type and concentration are the parameters studied in this research. 3-APTS is used in order to study the influence of temperature and reaction time on silanization process. For the study of the concentration and the silane structure influence, different silanes are probed such as: 3-APTS, 3-GPTMS, 2-AE-3-APTS (N-(2-aminoethyl)-3-(aminopropyltrimethoxysilane)) and 3-APMS (3-aminopropyltrimetoxysilane).

Thermal analysis and surface area measurements reveal that silane is not absorbed in CNFs surface with reaction times higher than 1 min. and reaction temperature higher than 25°C. Also, the silane adsorption is related with silane structure. Aminosilanes such as: 3- APTS and 3-APMS show similar behavior due to these silanes include the same functional group. However, the diaminosilane (2-AE-3-APTS) shows lower interaction with CNFs surface due to the length of the diamine chain, that avoid further silane adsorption on the coated CNFs surface. 3-GPTMS shows a similar behavior to other silanes at low concentrations, while for high concentrations multilayers are produced. Recently the same group (Nistal et al. 2011) reported other studies related with CNFs modified with vinyltryethoxy silane (VTS) and 3-MAT. The interactions between CNFs and silanes are analyzed by different techniques such as: TGA, FTIR, TEM, HRTEM, SEM and nitrogen adsorption. The TGA results indicate that similar silane concentration of VTS and 3-MAT form one and three silane monolayers, respectively. Authors also have shown that each silane produce different interactions with CNF. Thus, while in low silane concentrations, the vinyl group of VTS is bonded to the graphene CNF surface mainly through π–π interactions; 3-MAT link to CNFs through the carbonyl group with hydroxyl groups of graphene defect sheets; Silanol–CNF hydroxyl interactions are also expected at these silane concentrations. Silica layers also are detected by IR at 1250 cm^{-1} assigned to Si-O-Si vibrations. However, for high silane concentration, when the silica layer is formed, both silanes shown vinyl free and carbonyl free groups. This later is detected by the signals at 1370 and 1686 cm^{-1} in IR analysis, respectively. TEM and HRTEM images of these silanized carbon structures with 5% (w/w) of silane shown clear differences between CNFs and the same materials after silanization. TEM images are shown in the figure 10, there pristine CNFs present smooth surface (figure 10a) and the silane coating appears clearly for silanized CNF in the figures b–d. The 3-MAT coating seems less homogeneous, with localized increased thickness. HRTEM images of pristine and silane coated CNFs are also shown in Figure 11. Graphene layers of CNFs are observed in the case of pristine material. However, silane coated CNFs show thicker surfaces with low inner channels, mainly for the samples that are coated with 3-MAT (Figure 11b). It is clear that graphene layers are not observed at higher magnifications, showing that the silanes are coating the CNF surface. In addition, using Nitrogen adsorption, authors give evidence that each silane depend on the nature is adsorbed in different mode, inasmuch as, VTS is adsorbed essentially on graphene surface (defect free) and 3-MAT on the micropores with hydroxyl groups (defects zone).
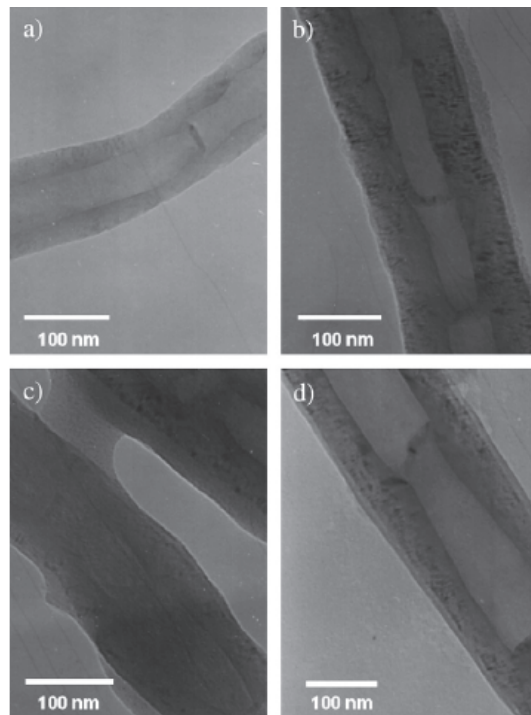
Fig. 10. TEM images; a) CNFs b-c) 3- MAT Silanized CNFs, d) VTS Silanized CNFs. Copyright Elsevier Science.
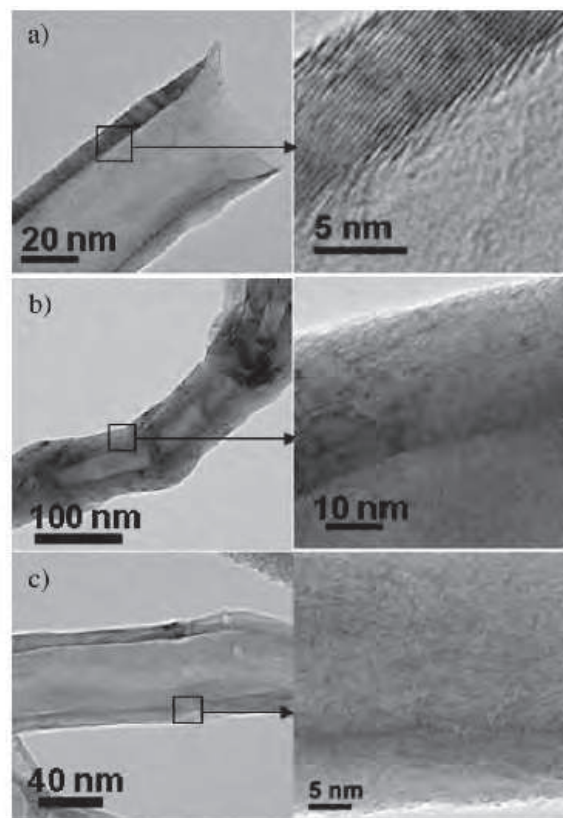

Fig. 11. HRTEM images; a) CNFs b) 3- MAT Silanized CNFs, c) VTS Silanized CNFs. Copyright Elsevier Science.

Silanization have also been used to attach optically active quaterthiophene molecules (T4) to graphene oxide sheets (Melucci et al. 2010). The procedure is achieved using a novel microwave-assisted silanization reaction. The method is useful to perform GO functionalization in one-step, under soft conditions in few minutes. The T4 molecules are linked to 3-APTS in order to form silane T4 moieties (T4-Si). The GO previously exfoliated in dimethylformamide (DMF) and T4-Si are introduced in a microwave oven reactor and irradiated at 80 °C (100 W) for 40 min. The hybrid GOT4 can be synthesized in either H2O or apolar organic solvents and deposited as single sheets, microplatelets or macroscopic membranes. Authors probe the properties of the new hybrid and the successful chemical functionalization considering a combined test of solubility and fluorescence. The hybrid properties for GOT4 are compared with its precursors: a mixture of GO and T4-Si without silanization reaction, and only GO. All suspensions are prepared in polar (DMF-H_2O 1:5 in volume) and apolar (DMF-CH_2-Cl_2 1:5 in volume) solvents. Suspensions are probed either normal light and under UV lamp showing different properties of the GOT4 hybrid as compared with GO and the mixture of T4-Si and GO. The figure 12 shows the GO-T4 membrane, the membrane observed with fluorescence microscopy and the suspensions under the two light types.
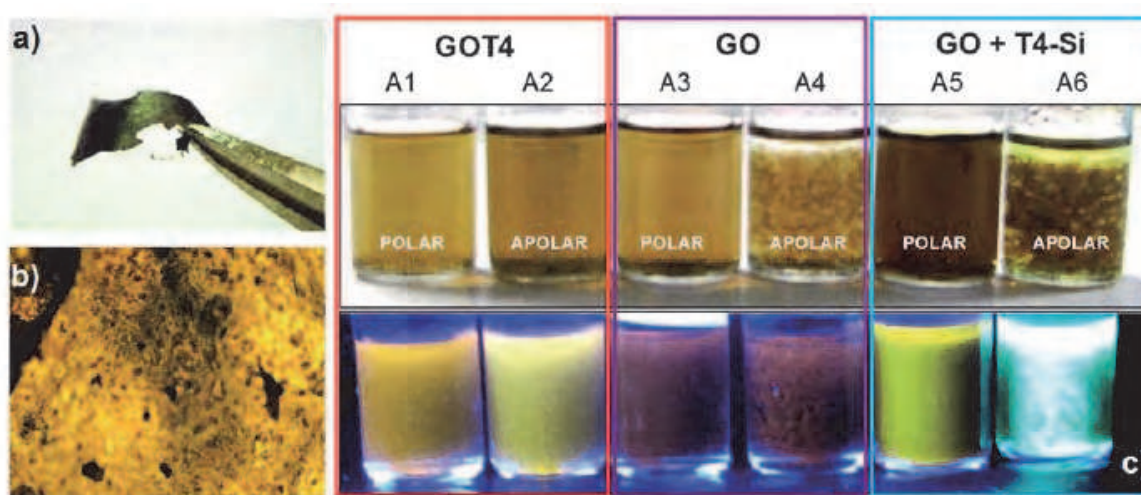

Fig. 12. GOT4 hybrids; a) membrane, b) image of GOT4 hybrid by fluorescence microscopy, c) Suspensions of GOT4, GO and GO + T4-Si in polar and apolar solvents under normal light (top) and UV lamp (bottom). . Copyright RSC.

Thus, silanization has started to establish it, as important protocol in order to attach organic moieties, biomolecules, polymers and other organic and inorganic groups that allow diversify carbon nanomaterials properties and possible uses. In this context, one of the first proposals to use silanization in CNTs is the specific and compatible interface in polymer nanocomposites. Next are reviewed the first results related with the silanization of CNTs and their incorporation in polymer matrices.

In spite of, there exist only few researches focus to use silanes as coupling agents in CNTs polymer nanocomposites (CNTPN), due to the versatility of silanization and the moieties that could be attached to CNTs and other carbon nanomaterials in the next years silanization follow being used as important chemical reaction in order to diversify carbon nanomaterials and improve their interaction with other materials.

6. Properties of polymer nanocomposites reinforced with silanized-carbon nanotubes

Recently, research focus to silanized CNTs has beginning to include these carbon nanomaterials in polymer matrices. As it has been mentioned one of the first propose of silanizing CNTs is improve the interface between carbon nanomaterials and the polymer matrices. The fact of incorporate different organic groups included in organosilanes to CNT surface is attractive to enhance the interactions at molecular level of nanomaterials with polymer. In addition, silanization could diversify properties of CNTs and therefore the features and possible applications of polymer nanocomposites. The selectivity of electronic properties and the behavior of CNTs depend on silane used, are some of the additional characteristics that also could be take in advantage in order to produce novel nanocomposites based on silanized CNTs. The easy application of silanization reactions to other carbon nanomaterials is an extra boon to considerer with a view to applied silanization to functionalize, diversify the properties and applications of different carbon

Polymer	Carbon nanomaterial type	Silane	Composites characterization	Reference
Epoxi	MWNT	3-Glycidoxypropyltrimethoxysilane (GPTMS)	TGA, DMA, three-point flexure test, compact tension test, dispersion and morphology, bulk electrical conductivity	Ma et al, 2007
Polyimide	MWNT	3-Isocyanatopropyltriethoxysilane (IPTES)	Dispersion and morphology, CP/MAS solid state ^{29}Si NMR spectroscopy, surface and volume electrical resistivity	Yuen et al, 2008 a
Polypropilene	MWNT	3-methacryloxypropyltrimethoxysilane (3-MAT)	Tensile test, morphology.	Zhou et al, 2008
Polyimide	MWNT	Vinyltriethoxysilane (PVTES)	Morphology, CP/MAS solid state ^{29}Si NMR spectroscopy, surface and volume electrical resistivities, tensile test.	Yuen et al, 2008 b
Silicone rubber (Sylgard®184)	MWNT	7-Octenyltrichlorosilane (7-OTCS) n-octyltrichlorosilane (n-OTCS)	Dispersion and morphology, indentation test,	Vast et al, 2009
High Density Polyethylene	Carbon nanofiber	Octadecyltrimethoxysilane	DMA, DSC	Wood et al, 2010
Ultra high molecular weight polyethylene	MWNT	3-Aminopropyltriethoxysilane (3-APTS)	Dispersion and surface morphology, wear test	Lee et al, 2010

Table 1. Polymer nanocomposites reinforced with silanized-carbon nanomaterials

materials including the nanocomposites field. Next are reviewed the advantages of silanized CNTs and CNFs on the development of polymer nanocomposites. Table 1 shows a resume of carbon nanomaterials silanized, the silane type, the polymer matrix used and the analyzed properties of polymer nanocomposites.

6.1 Electrical conductivity

One of the most outstanding properties of carbon nanomaterials is their electrical behavior. Carbon nanotubes or nanofibers posses π-bonds (C=C) that transfer electrical charges allowing a high electrical conductivity. Therefore adding small quantities of carbon nanomaterials to polymer matrix will reduce dramatically their surface and volume resistivity. This has been used in order to diversify the applications of polymer nanocomposites that could be since electronic devices to automotive and aerospace purposes. An extensive research with different kind of polymers has been done, giving many different conclusions about conductivity in nanocomposites that generate discrepancies between authors that have studied this phenomenon by years. In spite of divergence on results it is possible conclude that polymer matrix is not really a decisive factor in the electric response, in fact even when the nanocomposites are made with the same matrix the processing method can affect their electrical performance.

Research has shown that diverse factors can influence electrical behavior of nanocomposites, among the most important it is possible to mention the kind of nanomaterial structure: nanotubes (SWNT or MWNT), graphene sheets or nanofibers, their production method, dispersion technique, alignment inside the matrix, adhesion between nanomaterial and polymer, purification or chemical modification.

Regarding chemical modification, silane functionalization, as technique to improve dispersion and adhesion, also has important consequences in electrical conductivity of nanocomposites as was demonstrated by several authors.

Ma et al, 2007, evaluated the effects of silane functionalization of MWNTs on electrical properties of CNTs/epoxy nanocomposites. These authors utilize GPTMS as the functionalization agent; this silane is compatible with diglycidyl ether of bisphenol A (DGEBA), used as precursor of epoxy. The curing agent for this matrix was m-phenylenediamine. Nanocomposites with different weight fractions (0.05%, 0.10%, 0.25% and 0.50%) of the untreated CNTS (untreated-CNTs) and silane functionalized CNTs (silane-
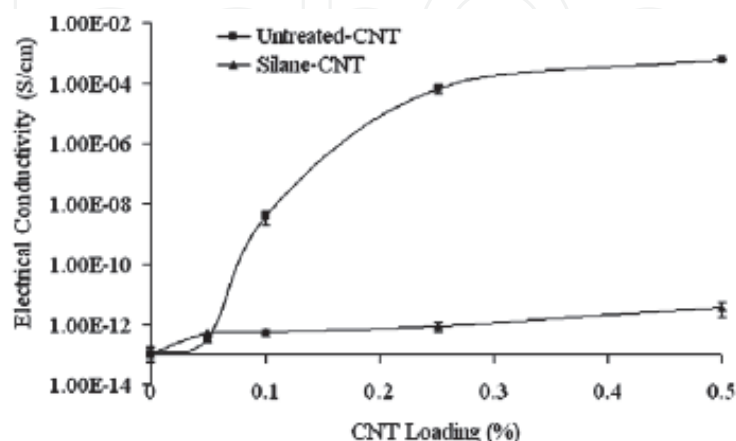

Fig. 13. Electrical conductivity for GPTMS-MWNTs epoxy nanocomposites. Copyright Elsevier Science.

CNTs) were evaluated. Figure 13 shows that percolation threshold for untreated-CNTs nanocomposite is around 0.1%, achieving the maximum electrical conductivity value (5.9 X 10^{-4} S/cm) with 0.50 %, whereas silane-CNTs nanocomposites only exhibit a very small increasing in conductivity. This behavior is explained taking into account that GPTMS molecules and epoxy endgroups are covalently bonded to the CNTs surface, these could react easily with the curing agent and produce wrapping of CNTs by the epoxy. This wrapping affects π-bonds and consequently charge transfer is also perturbed. The authors also conclude that a better dispersion of CNTs in polymer matrix is unfavorable to the creation of electrical networks.

On the other hand, Yuen et al, 2008, showed that chemical modification of MWNTs with silane improves electrical behavior of polymer nanocomposites. In this research, the authors use acid-modified MWNTs and IPTES-modified MWNTs, for these last also acid-modified MWNTs were prepared as base material. Three ratios in weight of IPTES to acid-modified MWNTs were used: 1:1 (IPTES-MWCNT-1[1]), 2:1 (IPTES-MWCNT-2) and 3:1 (IPTES-MWCNT-3). All these were included in polyamic acid, which acts as polyimide precursor. Mixture of modified-MWNTs (with acid and with IPTES) and polyamic acid was heated to 300 °C, temperature for imidation reaction; at this point the IPTES molecules attached to MWNTs surface react and connect other MWNTs, thus an IPTES-MWNTs network is achieved, as is shown in figure 14. This network reduces the electrical resistivity and provides desired effective electrical pathways. Figure 15 a-b shows surface and volume electrical resistivity of the IPTES-MWNT/polyimide composites. As can be observed the acid-MWNTs nanocomposites exhibit the highest values for both surface and volume resistivity when 6.98 wt% concentration was used, whereas at the same concentration IPTES-MWCNT-3 nanocomposites have the low resistivity value. These results show that silanization could be a useful technique to improve conductivity of CNTs polymer nanocomposites if a MWNTs network is formed. In contrast to when IPTES content was low and no more than 2.44 wt% of MWNTs was used, the network was not produced and MWNTs may be isolated, this means well dispersed, this fact causes higher values in volume resistivity.

Similar results with polyimide matrix were obtained using PVTES-modified MWNTs (Yuen et al, 2008 b). In this study three ratios in weight of VTES to unmodified MWNTs were used: 1:1 (VTES-MWCNT-1[2]), 2:1 (VTES-MWCNT-2) and 3:1 (VTES-MWCNT-3). The nanocomposites were synthesized using polyamic acid as polyimide precursor. Electrical behavior, depicted in figure 16, shows that unmodified MWNTs nanocomposites need high concentrations of CNTs in order to achieve low volume resistivity, however VTES-modified nanocomposites reach the percolation threshold with only 2.44 wt% of CNTs. These results were attributed to connections between VTES-MWNTs that can occur during imidization reaction.

Accordingly with these results, electrical conductive properties of polymer nanocomposites reinforced with silanized-carbon nanotubes depend on network formation; consequently increase in the dispersion does not improve conductivity nor decrease the percolation threshold. However other important properties, such as thermal stability or thermo-mechanical behavior, are closely dependent on dispersion features.

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[1] The original nomenclature in the figure given by Yuen et al, 2008a is maintained in order to avoid confusions if the article is consulted. MWNCT appear instead of MWNTs

[2] The original nomenclature in the figure given by Yuen et al, 2008b is maintained in order to avoid confusions if the article is consulted. MWNCT appear instead of MWNTs
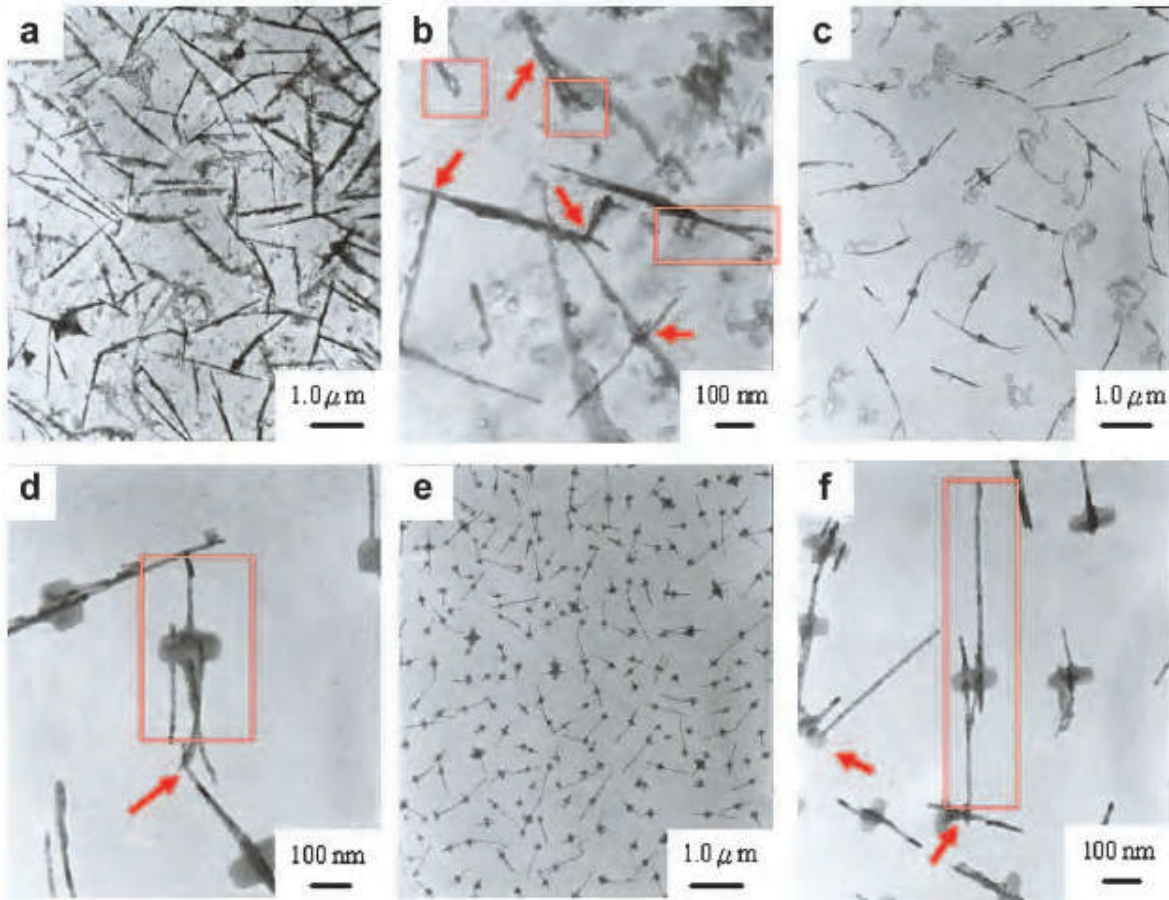
Fig. 14. TEM images of 6.98 wt% IPTES-MWNT polyimide nanocomposites, a)
IPTES:MWCNT-1 (10,000X), b) IPTES:MWCNT-1 (50,000X), c) IPTES:MWCNT-2 (10,000X),
d) IPTES:MWCNT-2 (50,000X), e) IPTES:MWCNT-3 (10,000X), f) IPTES:MWCNT-3
(50,000X). The arrows show connected MWNTs by IPTES molecules. Copyright Elsevier
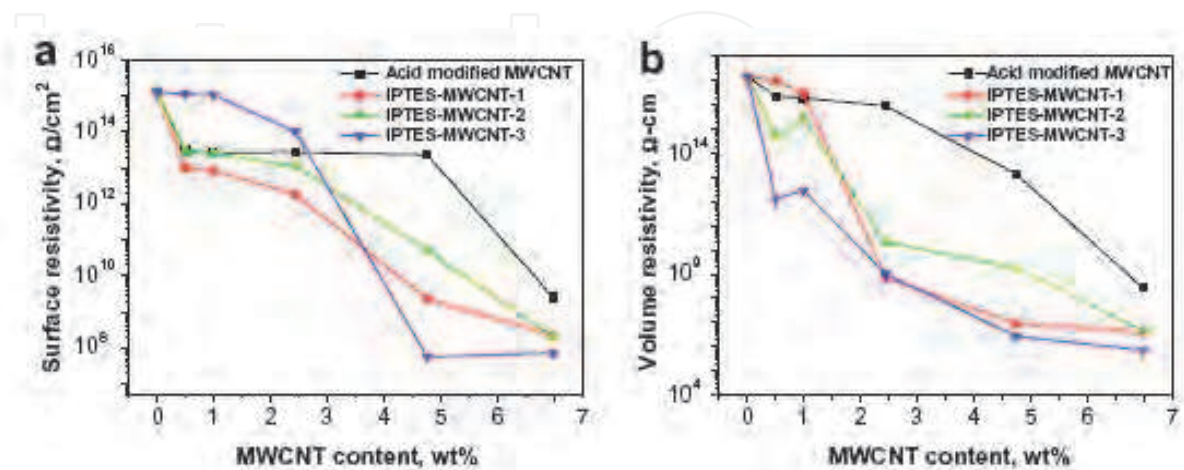Science.

Fig. 15. Electrical behavior of acid and IPTES modified MWNTs poyimide nanocomposites,
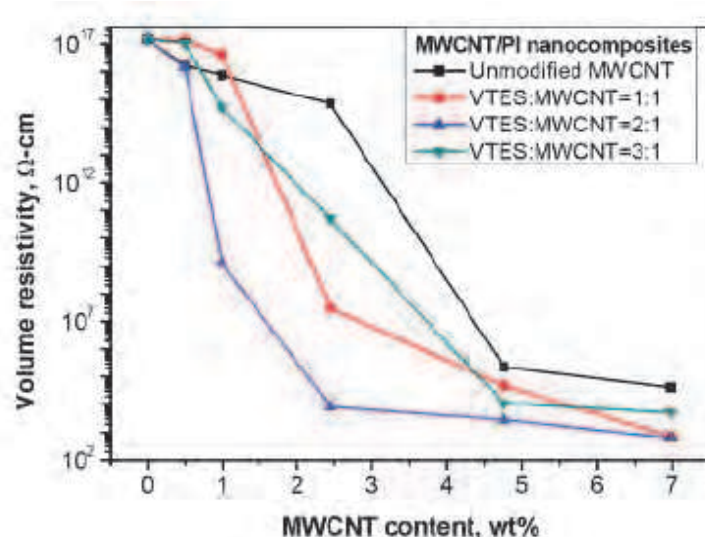a) Surface resistivity, b) Volume resistivity. Copyright Elsevier Science

Fig. 16. Volume resistivity of VTES-MWNTs polyimide nanocomposites. Copyright Wiley Periodicals Inc.

6.2 Mechanical properties

It is well known that CNTs have outstanding mechanical properties, however as well as in other kind of composites good interfaces and dispersion of reinforcements are needed to take full advantage of this feature. Nanometric reinforcements have interactions at molecular level, increasing synergic effects between matrix and nanostructures, thus only small quantities of CNTs can increase drastically the mechanical properties of nanocomposites when interfacial contacts and good dispersion are achieved. In fact, reinforcement properties in CNTs polymer nanocomposites involve optimal transfer of strain between matrix and CNTs. This implies a strong interfacial bonding at nanometric level. A useful procedure to get this challenge is to cause that CNTs form covalent bonds during the polymerization process and have them chemically integrated in the cross-linked matrix. Silanization provides functional chemical interactions to CNTs in order to reach these conditions, this have been probed by several authors.

GPTMS-MWNTs in epoxy matrix cause higher elastic modulus than the untreated-CNTs epoxy nanocomposite, over the entire range of CNTs content studied (from 0 to 0.5 wt %). Also the flexural strength of these nanocomposites has a similar tendency (Ma et al, 2008). Compact tension tests provide interesting results for these GPTMS-MWNTs nanocomposites. The quasi-static fracture toughness (K_{IC}) evaluated with this study show a continuous decrease when untreated-CNTs were used, in contrast to nanocomposites with GPTMS-MWNTs. The use of silanized-MWNTs increases K_{IC} values with CNTs content. Ma et al, 2008, explained this behavior considering that untreated-CNTs have poor dispersion in the epoxy matrix, in addition to few interfacial interactions. After silane functionalization, both conditions were improved by the attachment of silane molecules onto CNTs surface.

Vast et al, 2009, used two types of silane: 7-OTS and *n*-OTCS, which differ only by the nature of their end groups. These were used in order to compare dispersion of purified and silanized MWNTs in a thermally curable silicone rubber: Sylgard®184 and the effect on the Young's modulus. The authors considered that silane act by two ways simultaneously, they graft on the MWNTs and also they form siloxane networks on MWNTs surface through condensation with nearby silane molecules. In addition the chemical structure of the

siloxane network on the silanized-MWNTs is very similar to vinyl-terminated PDMS chains and methylhydrosiloxane copolymer chains (both are precursors of silicone rubber), this fact is favorable to achieve well silanized-MWNTs dispersion. The results in this research show that chemical structure of silane has a strong influence in dispersion and mechanical performance. Rubber nanocomposites with n-OTCS-MWNTs exhibit poor dispersion that is reflected by reduced mechanical properties, since pristine silicone rubber itself has a better Young's modulus. In effect, increasing the n-OTCS-MWNTs content gives even poor mechanical behavior, this is due to growth of big aggregates causes Young's modulus to decrease significantly. In contrast to this effect, 7-OTCS-MWNTs rubber composites show an important increasing in Young's modulus, since it increases from 6.7 MPa for pristine rubber to 9.9 MPa only with 0.2 wt% of silanized-MWNTs. This fact is attributed to silane interactions because of purified-MWNTs modulus increases slightly, reaching only 7.7 MPa with 0.5 wt% content of MWNTs.

Yuen et al, 2008, also have studied the effect of silanized MWNT's in the polymer crosslinking process. In this case they used VTES that is covalently attached to MWNT's surface by free radical reaction.VTES-MWCNTs[3] were added to the polyamic acid (imide precursor) and then the mixture was heated until 300 °C was reached. Tensile test results show that when unmodified MWNTs were used, the tensile strength of the MWCNT polyimide composite was increased 19% compared to neat polyimide. However, as can be observed in figure 17, VTES-MWCNT's polimide nanocomposites show better mechanical behavior, since all the samples have higher values in tensile strength, with exception of 7 wt % of VTES:MWCNT=3:1. The highest tensile strength (165 MPa) was reached with two VTES:MWCNT nanocomposites: 1:1 and 2:1, both with only 0.5 wt % of modified CNTs content, but beyond this concentration tensile strength decreases gradually. On the other hand Young's modulus for pure polyimide is around 2.3 GPa and increases gradually with unmodified-MWNTs content until reach 3 GPa with 7 wt%, whereas with VTES-MWNTs the Young's modulus increases considerably, reaching a maximum value of 5.5 GPa with VTES:MWCNT=1:1. In accordance with these authors, VTES:MWCNTs ratio has an important effect in nanocomposite performance. VTES was grafted on MWNTs most effectively with 2:1 ratio. However, 3:1 ratio allows grafting but leaves VTES free to interact during cross linking polymerization. Therefore, for Young's modulus, VTES-MWNTs=3:1 shows the highest values over all range of contents, and with 7 wt % has the second better one. This occurs due to free VTES groups connect VTES-MWCNTs with Si-O-Si bonding, causing evident increasing in Young's modulus and brittleness of the composites.

Nanocomposites are made with an extensive variety of polymers, such as epoxi, polyimide or rubber, mentioned before, where it is possible to take advantage of polymerization reaction in order to achieve an adequate dispersion of MWNTs. But also other processing techniques can be used with interesting results. For instance, Zhou et al, 2008, prepared blends of polypropylene and silanized-MWNTs by using a rheometer at 190 °C for 10 min and a rotor speed of 75 rpm. The contents of MWNTs in these blends were: 0.25 wt%, 0.5 wt%, 1 wt% and 2 wt%. Once mixed, the silanized-MWNTs–polypropylene blends were molded by compression at 190 °C to form nanocomposite sheets. Before mixing, the MWNTs were silanized using 3-MPTS. The effects of silanization treatment and CNTs content on the tensile properties of polypropylene nanocomposites were studied. Tensile

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[3]The original nomenclature given by Yuen et al, 2008b is maintained in order to avoid confusions if the article is consulted. MWNCT appear instead of MWNTs.
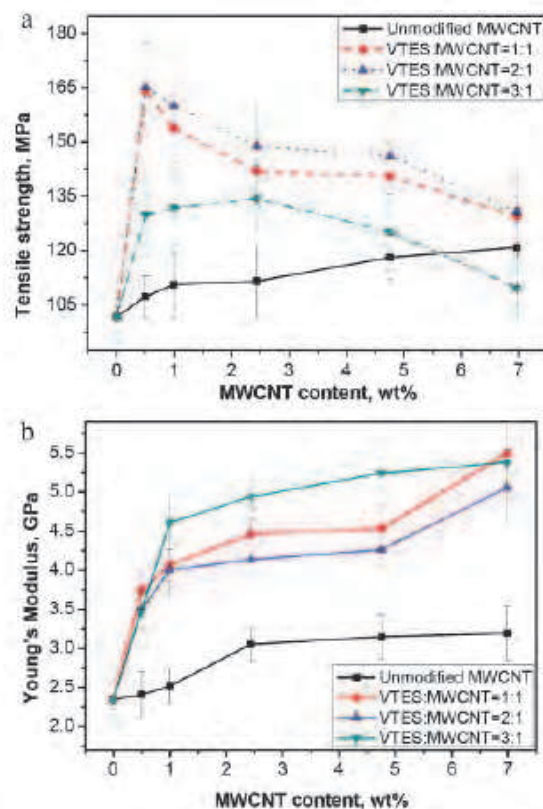
Fig. 17. Effect of VTES:MWCNT ratio and MWCNT content on the mechanical properties of polyimide nanocomposites, a) Tensile strength, b) Young's Modulus. Copyright Wiley Periodicals Inc.

strengths for all percentages of CNTs content were high when 3-MPTS-MWNTs were used. The highest value was around 39.5 MPa with 1 wt%, this means and increasing of 10% with respect to pure polypropylene. Unmodified MWNTs only increase the tensile strength in almost 6% for the same content of MWNTs. Homogeneous dispersion is severely influenced by concentration of CNTs, low quantities of 3-MPTS-MWNTs or unmodified-MWNTs allow that partial tensile strain can be transferred to CNTs, producing increments in tensile strength until 1 wt% of MWNTs content is reached. Furthermore, if higher quantities of CNTs are used the tensile strength of polypropilene nanocomposites decreases due to agglomerates of MWNTs are formed.

Tribology deserves a special mention among the mechanical properties. The tribological properties of polymers are usually improved if some reinforcements are used, likewise mechanical properties. However, there is a lack of information regarding this theme. In fact, understanding the tribology of polymers is not easy, since these have complicated multiphase structures with multiple domains and subdomains in which their mechanical behavior varies significantly, in addition polymers are viscoelastic, and this implies that their properties change with time, as was described by Brostow et al, 2006 and 2008. In spite of these difficulties, Dasari et al, 2009, published a complete and interesting review with important results on wear and scratch damage in polymer nanocomposites, however they do not mention any functionalization treatment, not even silanization. To the date, almost all authors in silanized-CNTs polymer nanocomposites deal with mechanical properties, but they do not include tribological data among their results.

One of the few results on this area was reported by Lee et al, 2010, they studied specifically friction coefficient and wear rate of 3-APTS-MWNTs in ultra high molecular weight polyethylene (UHMWPE). These authors demonstrated that silanized CNT/UHMWPE nanocomposites have better dispersion and stronger interfacial bonding than oxidized-MWNTs, this fact is reflected in an evident lower friction coefficient for silanized-MWNTs nanocomposites. Besides, as figure 18a shows, the maximum values for depth profile were those corresponding to raw UHMWPE and oxidized-CNT for all sliding speed range, these results are in agreement with wear rate, which confirm that silanized CNT/UHMWPE nanocomposites have a better performance. The wear rate of these nanocomposites decreased around 83, 53 and 59 %, respectively at sliding speeds of 0.12, 0.18 and 0.24 m/s, compared with the raw UHMWPE.

SEM images in figure 18 shows wear tracks (indicated by arrows) in raw polymer and nanoreinforced composites. There are severe damages in raw polymer, such as wear debris, cracks and exfoliation, but these diminish evidently for oxidized CNT/UHMWPE nanocomposite, and even more for silanized CNT/UHMWPE, corroborating thus an improvement in CNT dispersion and interfacial interactions between CNTs and polymer matrix because of silane treatment of CNTS.
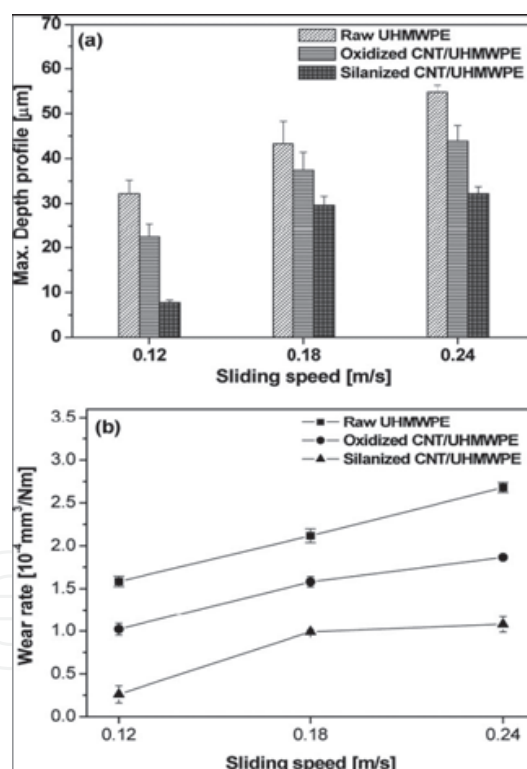

Fig. 18. Tribological behavior of raw UHMWPE, oxidized CNT/UHMWPE and silanized CNT/UHMWPE nanocomposites, a) Maximum depth profile, b) Wear rate. Copyright Wiley InterScience.

Certainly, it is evident that, as well as other mechanical properties, tribological behavior needs to be exhaustively studied, since results until now are not conclusive, as was described by Dasari et al, 2009. In addition to their concern, also it is worthy to take into account that different kinds of functionalization, such as silanization, play an essential role

to take advantage of dispersion and interfacial interactions and thus to improve polymer nanocomposite performance.
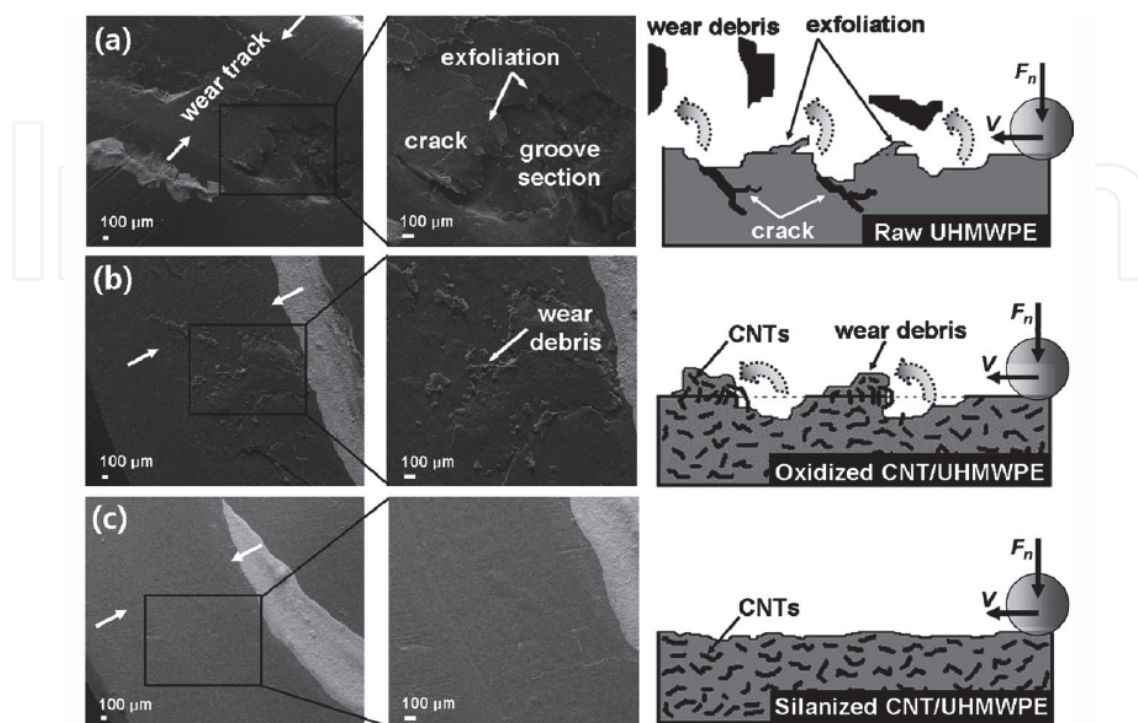

Fig. 19. SEM images and schematic illustration of worn surface, a) raw UHMWPE, b) oxidized CNT/HMWPE nanocomposite, and c) silanized CNT/UHMWPE nanocomposite. Copyright Wiley InterScience.

6.3 Dynamical mechanical analysis

The evaluation of thermomechanical properties in polymer nanocomposites is an important parameter in order to estimate the performance of these kinds of materials. The elastic behavior and the movement of chains related with thermal transition can be evaluated by Dynamical Mechanical Analysis (DMA). The interactions produced between CNTs and polymer matrix also can be evidenced by the results obtained by this technique indicating if functionalization produces some changes as compared with not functionalized materials.

In spite of, the relevance of DMA in Carbon Nanotube Polymer Nanocomposites CNPNs, only few researches that involve polymer matrix reinforcement with silanized CNTs or silanized carbon nanomaterials, have reported this behavior. Ma et al. 2007 evaluate thermomechanical properties of Epoxy composites reinforced with MWNTs silanized with 3-GPTMS. Epoxy is reinforced with silanized CNTs at different concentrations. Figure 20 show the results of polymer nanocomposites including silanized CNTs. Nanocomposites with untreated CNTs present lower storage modulus that epoxy matrix at 30 °C. However at the same temperature, nanocomposites reinforced with silanized CNTs show a slight increment in storage modulus as compared with the modulus of Epoxy. Authors, indicate this behavior as better dispersion of silanized CNTs than untreated CNTs in polymer matrix. At high temperature both nanocomposites with silanized and untreated CNTs improve notably the storage modulus; but, the values in tang delta indicate more slippages

between CNTs and polymer in nanocomposites with untreated CNTs than those containing silanized CNTs (figures 20 b, d). This effect is attributed cross-linking reactions of epoxy and hardener promoted by silanized CNTs. Thus, the link between the silane-treated CNT and epoxy effectively change the movement of molecular chains reflected in Tan Delta.
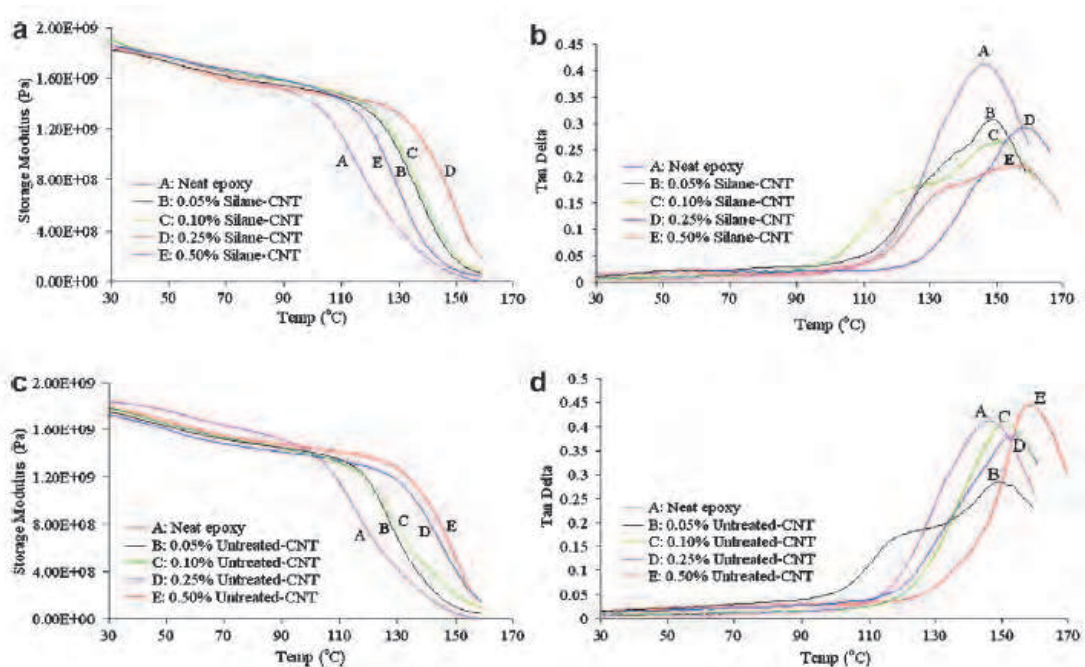

Fig. 20. Dynamical Mechanical Analysis of polymer nanocomposites reinforced with CNTs and silanized CNTs (3-GPTMS). a,c) Storage Modulus; b,d) Tan Delta. Copyright Elsevier Science

Other researches (Wood et al. 2010) that involve DMA of Polymer Nanocomposites containing silanized CNFs with different silane treatments have found that silane reaction assisted by NaOH improve the interactions at interface level more than only silanization. Therefore, the storage modulus at -70 °C of polymer nanocomposites reinforced with silanized CNFs increase 39 % with respect to polymer matrix (HDPE High Density Poly ethylene) . Storage modulus at 25 °C also increase in 20% for the CNPNs reinforced with silanized CNTs assisted by NaOH as compared with HDPE. Nanocomposites containing silanized CNTs but, where the reaction is not assisted by NaOH, only increase the storage modulus at 70 °C in 6 % with respect to HDPE and storage modulus for these composites is not increased at 25 °C.

Recently, in our group (Velasco-Santos et al. 2011) DMA have been used to evaluate CNPNs reinforced with 1 wt% of silanized CNTs (3-MAT) in Poly (methyl methacrylate) (PMMA) matrix. Storage modulus of CNPNs with modified CNTs (1 wt%) at 30 °C increases 150 % with respect to PMMA and CNPNs synthesized with untreated CNTs (1 wt %) only increase 82 %. In addition, the storage modulus at 90 °C is almost three times for composite with silanized CNTs as compared with composite reinforced with untreated CNTs. Thus, in spite of there are some reports that involve the evaluation of CNPNs reinforced with CNTs functionalized by silanization; a lot research that evaluates thermomechanical properties of CNPNs modified with CNTs functionalized with different organosilanes is needed. Successful silanization provide to CNTs diverse properties including compatibility and

undoubtedly DMA is very important technique to evaluate interface, chains movement, transitions and storage and loss modulus. DMA have been employed for other systems than involve the evaluation of CNPNs modified with organosilane but do not involve interaction of organic moieties of the silane with polymer matrix. For instance, Silica-coated multi-walled carbon nanotubes (MWCNT@SiO2) were synthesized by a sol–gel method and then incorporated into an epoxy matrix (1 wt%) by Cui et al 2011. The storage modulus of CNPN with modified CNTs improves slightly with respect to CNPN with unmodified CNTs and epoxy. However the increase is maintained constantly since 30 °C until 140 °C

7. Conclusion

Silanization is a single chemical functionalization process that is effective to modify CNTs surface and properties. The reaction could be achieved after oxidation or directly on CNT surface by sylilation and hydrosilylation. Silanization type and oxidation process play an important role in the final properties of silanized- CNTs. Taking in count previously results of silanization, it is possible that the combination of soft oxidation and redox or initiation reactions also could yield silanized carbon nanotubes.

The control of this kind of chemical modifications on CNTs, depending on the organosilane used; is useful to manage electronic features of CNTs, and therefore diversify the electrical conductivity and related properties of silanized CNTs. The field of silanizing carbon nanomaterials in order to diversify their properties is a new open gate with interesting opportunities.

Moreover, silanization is functional method to modify chemically other carbon nanostructures such as graphene oxide and carbon nanofibers and could be applied to other carbon nanoforms with sp^2 graphitization. The opportunity to use organosilanes to diversify carbon nanomaterial characteristics and properties is other field that could be exploited.

Results reviewed here show that successful silanization change the surface behavior of CNTs and depending on the organic moieties in the organosilane used, the interaction of CNTs with different polymer matrices can be improved, as was suggested by our group some years ago. Recently, silanized CNTs incorporated to diverse polymers have shown interesting, electrical, mechanical, thermal and thermomechanical properties that can be improved or diversifying in the CNPNs synthesized.

Thus, silanization is shown as single chemical reaction that is useful to modified and diversify carbon nanomaterials properties, and work as effective coupling agent to develop polymer composites. However, the versatility of the silane moieties could be effective to diversify even more the applications of organosilanes in other systems or composite types. Chemical of carbon nanomaterials provide other possibilities that not are possible in macroscopic materials.

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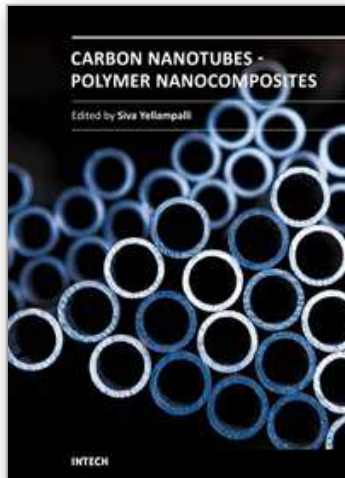
Carbon Nanotubes - Polymer Nanocomposites

Edited by Dr. Siva Yellampalli

Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This books focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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