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Silanization and silica enrichment of multiwalled carbon nanotubes: Synergistic effects on the thermal-mechanical properties of epoxy nanocomposites

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ABSTRACT

In this paper the synergistic effects of both 3-amminopropryltriethoxy silane (APTES) functionalization and silica enrichment of carbon nanotubes on thermal and thermal-mechanical properties of epoxy based composite materials were investigated. Pristine multiwalled carbon nanotubes were oxidized, functionalized with APTES and then modified with silica nanoparticles preformed through the Stober process. The FTIR, XPS and TGA analysis confirmed the occurrence of the silane functionalization and surface silica enrichment. TEM analysis showed the presence of a "bunches" morphology where silica nanoparticles aggregated around both the CNTs wall and their ends. Thermo-mechanical, thermal and flammability properties of nanocomposite containing 1 wt% of different fillers were determined and results compared to neat epoxy resin.

Results showed that both the elastic and rubbery modulus increase with the addition of filler. In particular, in the rubbery region, the storage modulus of composites with silanized and silica enriched carbon nanotubes were about 240% and 285% higher than modulus of neat epoxy system. In the glassy region, a modest increment of 25% for the storage modulus was recorded. The glass transition temperature increased of about 20 °C with silica enriched carbon nanotubes alongside with a significant enhancement of the damping behavior.

1. Introduction

In the last years, nanotechnologies are pushing the designing and engineering processes of novel multifunctional materials with unusual or improved properties. In this respect, carbon nanotubes (CNTs) have been widely investigated as reinforcing filler in polymer matrix due to their unique atomic structure, very high aspect ratio and outstanding mechanical properties [1,2]. The level of understanding of CNT reinforcement mechanism in polymer hosting matrix is still elusive and literature data are often very puzzling [3,4]; however, it has been widely recognized that both carbon nanotubes dispersion and interfacial bonding with the polymer matrix are the key parameters which need to be considered for enhancing the properties of the resulting polymeric composites.

The modification of the surface structure of CNTs through chemical-grafting, including amino-functionalization [5,6], β-hydroxyester surface functionalization [7] and silanization [8,9] reactions are the most effective methods to improve the CNT compatibility as well as the dispersion within the polymeric matrix. The surface chemical modification of CNTs is generally made through preventive

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oxidation processes, which induce the formation of acidic and hydroxyl groups on the surface, making it possible to bind several organic moieties [10]. Moreover this treatment leads to the formation of numerous defects on both the CNT tip-end and sidewalls with the consequent breaking up of the CNTs as well as reduction of the aspect ratio [11,12], which is generally detrimental for mechanical and electrical properties of nanocomposites. In this respect the silanization of CNTs has been shown to be a valuable approach for compensating the reduction of CNTs aspect ratio resulting from chemical treatments. Firstly Ma et al. [13] and Velasco-Santos et al. [14] have studied the silanization of MWCNTs by using 3-glycidoxypropyltrimethoxysylane and 3-mercaptopropyltrimethoxysilane. In these systems the silane molecules were mainly anchored to the CNT surface through the interaction of silanol or alkoxyde groups with hydroxyl groups on the carbon nanotubes produced by oxidation process. Kathi et al. [15] and Lee et al. [16] showed that the MWCNTs functionalized with 3-aminopropyltriethoxysilane enhanced the performances of epoxy based composites in terms of high dimensional stability at elevated temperatures, excellent thermal and chemical resistance, high mechanical strength and ease of processing.

Among the several approaches widely adopted for the designing of multifunctional materials, one of the most interesting is the study of the synergistic effects arising from the simultaneous presence of nanoparticles with different aspect ratio. For example, the incorporation of both clay and MWCNT in acrylonitrile–butadiene–styrene terpolymers (ABS) has been shown to significantly slow down the combustion reactions compared to the systems filled simply with clay or MWNTs. The CNTs act as a sealing agent that connect clay layers and reduce surface cracks in the char produced, leading to an enhancement of the barrier to the evolved flammable volatiles and to oxygen ingress into the condensed phase [17]. As for the electrical properties, a recent work of Sumfleth et al. [18] is focused on the systems based on epoxy resin filled with MWCNTs and carbon black particles. Due to the presence of carbon black particles, which shortcut the MWCNT branches, it was possible to preserve the electric conductivity by reducing the amount of carbon nanotubes. Increased electrical conductivity was also found in epoxy nanocomposites obtained by using carbon black (CB) and silica [19] or MWCNT and graphite nanoplatelets [20]. Beyond the simultaneous presence of nanoparticles with different aspect ratio, another innovative approach is that based on the use of nanoparticles whose surface has been suitably functionalized. It has been recently proven that the simultaneous presence of carbon nanotubes functionalized with both vinyltriethoxysilane and 3-isocyanotopropyltriethoxysilane along with siloxane domains obtained through sol–gel method into an epoxy resin allows the enhancement of the thermal stability and the flame retardance of the nanocomposites as well as a substantial increment of T_g and an improvement of mechanical properties [21,22].

On this basis, in the present study, multiwalled carbon nanotubes functionalized with 3-amminoproprylriethoxy silane (APTES) and enriched with silica nanoparticles forming a "bunches" structure, have been proposed as innovative filler for the preparation of epoxy nanocomposites with enhanced thermomechanical properties. Oxidized multi-walled carbon nanotubes were functionalized through silanization with 3-aminopropyltriethoxysilane by using *N,N′*-dicyclohexylcarbodiimide (DCC) catalyst to promote the formation of amide bonds with the silane as pendants. The APTES functionalized MWCNTs were further modified with hydroxylated silica nanoparticles previously produced by using the Stober method. The extent of chemical functionalization and silica enrichment of carbon nanotubes was investigated by FT-IR analysis, X-ray photoelectron spectroscopy, scanning electron microscope and transmission electron microscope analysis. The nanocomposites obtained by dispersing 1 wt% of acidic functionalized, APTES functionalized and silica enriched MWCNTs in the commercial epoxy resin (CYCOM 977-20) were characterized by dynamic mechanical analysis (DMA), thermal analysis (TGA), thermal mechanical analysis (TMA) and calorimetric cone.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) produced by chemical vapor deposition (CVD) were purchased from Nanocyl S.A., Belgium. The nominal diameter is 9.5 nm, the length ranges from 1 to 10 μm and the purity is above 95%. 3-aminopropyltriethoxysilane (APTES) and tetraethyl orthosylicate (TEOS) with purity respectively of 98% and 99% was purchased from Sigma–Aldrich, USA. Nitric acid (65%), *N,N′*-dicyclohexylcarbodiimide (DCC), ammonium hydroxide solution (31.5% NH_3), dimethylformamide (DMF) and all solvents were also purchased from Sigma–Aldrich and used without purification.

The epoxy matrix used in this work is a one-part liquid epoxy resin commercially available under the trade name of CYCOM 977-20 by Cytec Engineered Materials.

This epoxy system is a high molecular weight resin usually used for aerospace structural elements and it does not contain any thermoplastic fillers as toughening agents. The liquid system has a low viscosity (50 cP) to allow the resin transfer molding process at temperatures between 60 and 85 °C. The density and the T_g (as maximum of tanδ) of the solid cured resin are 1.31 g/cm^2 and 212 °C, respectively. Further physical properties as from technical datasheet are the followings: tensile strength 81.4 ± 11 MPa, tensile modulus 3.52 ± 0.14 GPa, flexural strength 197 ± 7 MPa and flexural modulus 3.45 ± 0.07 GPa.

2.2. Oxidation of multi-walled carbon nanotubes

Two hundred milligrams of MWCNTs was dispersed in distilled water for 30 min by using a Sonicator S3000 (Misonix). The resulting dispersion was refluxed in 10 ml of nitric acid (65%) at 120 °C for 3 h. After centrifugation the solid sample was washed repeatedly with deionised water and then dried under vacuum at 80 °C for 24 h. The multi-walled carbon nanotubes obtained from oxidation treatment were labeled as MWCNT-COOHs.

2.3. Silanization of MWCNT-COOHs with 3-aminopropyltriethoxysilane

Two hundred mg of MWNT-COOHs was dispersed in 100 mL of dimethylformamide and sonicated for 1 h. Afterwards 44 mL of APTES and 62 mL of a 1 M *N,N′*-dicyclohexylcarbodiimide (DCC) solution were added. The resulting dispersion was mixed for further 3 h at 40 °C in an inert atmosphere. The obtained APTES functionalised multi-walled carbon nanotubes (coded MWNT-APTESs) were collected by filtration and dried under vacuum at 80 °C for 24 h [23]. In this procedure the DCC was used to promote the direct reaction between carboxylic acid and amine APTES groups to form amide groups rather than the formation of –SiOMWCNT bonds as described in literature [15,24]. In details the negatively charged oxygen of carboxylic acid groups reacts, as a nucleophilic agent, with the central carbon in DCC and forms a highly electrophilic intermediate which makes the reaction with the terminal amino group of APTES more efficient.

2.4. Preparation of surface hydroxylated silica nanoparticles

Surface hydroxylated silica nanoparticles were prepared by using the Stöber process through the hydrolysis and condensation of TEOS in ethanol, and in presence of ammonia as the catalyst [25]. In details 250 mL of ethanol and 17.5 mL of ammonia solution (30% NH_3) were mixed and stirred at 90 °C for few minutes. Afterwards, 7.5 mL of TEOS was dropped into the solution and the system was kept at 90 °C for 3 h. The colloidal dispersion was cooled at room temperature and purified by using dialysis membranes (Dialysis Tubing Cellulose Membrane, size: 43 × 27 mm from Sigma Aldrich) to remove the oligomers and unreacted species. The purification treatments were carried out at room temperature for one week renewing the external solution with purified water, once a day. The size distribution of surface hydroxylated silica nanoparticles dispersed in water was determined by dynamic light scattering analysis-DLS. The nanoparticles exhibit a bimodal size distribution for the presence of both particles with radius in the region 2–10 nm and particles with radius from 40 to 200 nm. The smaller particles are more abundant than larger silica particles (see Fig. 1).

2.5. Enrichment of MWNT-APTESs with silica nanoparticles

The superficial enrichment of multiwalled carbon nanotubes with silica nanoparticles was obtained by reacting the hydroxyl groups of surface hydroxylated-silica nanoparticles with ethoxysilane of MWNT-APTESs. In details 5 mg of MWNT-APTESs was dispersed in 15 ml of ethanol and sonicated for 30 min at room temperature. Then 50 ml of surface hydroxylated silica particles was added to the solution and sonicated for further 30 min. The resulting nanotubes superficially enriched with silica nanoparticle (coded MWNT-APTES-$SiO_{2-x}(OH)_x$) were obtained by filtration (200 nm-pore polycarbonate, Millipore) and drying under vacuum at 80 °C for 24 h.

A pictorial representation of the multiwalled carbon nanotubes functionalised with acidic moieties (MWCNT-COOHs), aminosilanes (MWNT-APTESs) and enriched with hydroxylated silica particles (MWCNT-APTES-$SiO_{2-x}(OH)_x$) is shown in Scheme 1.

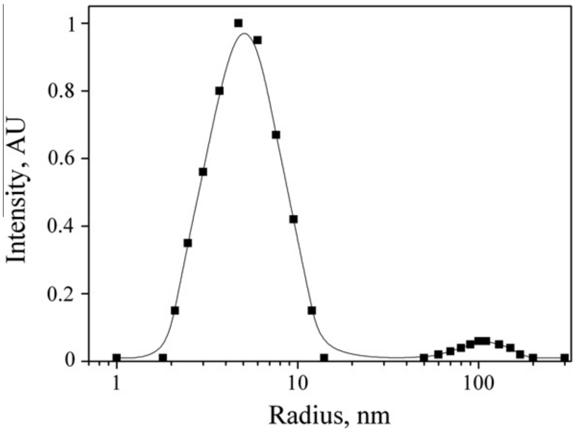


Fig. 1. Size distribution of silica particles prepared by Stöber method.

2.6. Preparation of epoxy based nanocomposites

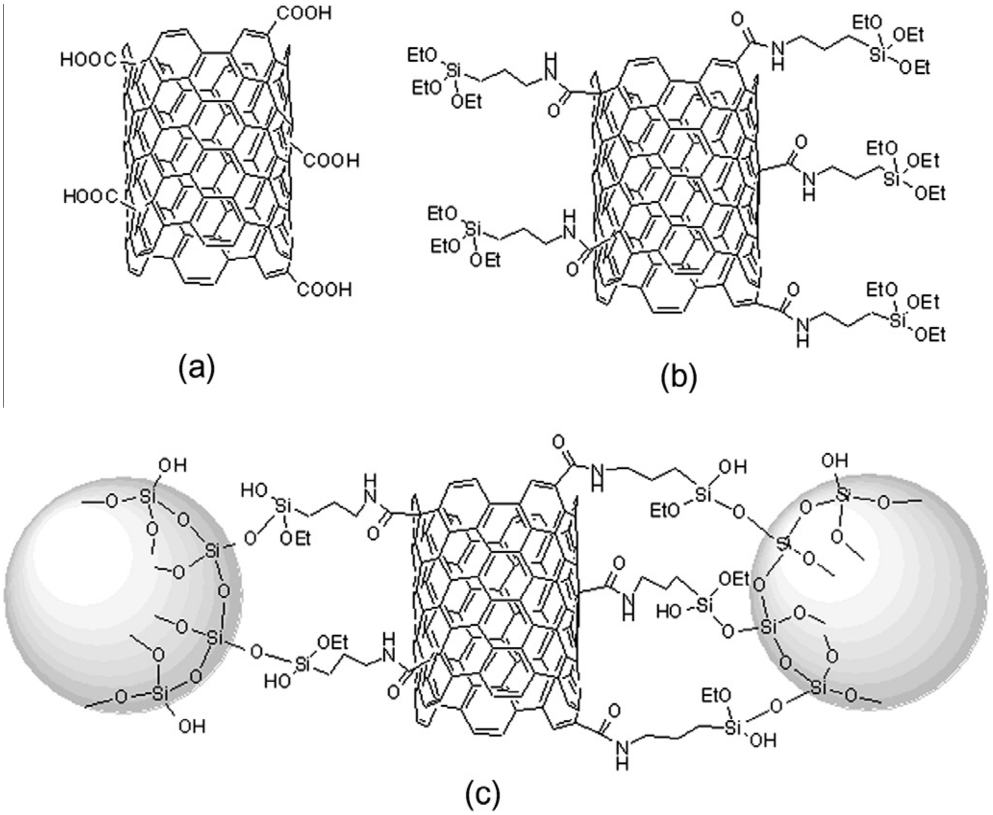
Surface hydroxylated silica particles obtained from Stöber process, MWCNT-COOHs, MWCNT-APTESs and MWCNT-APTES-$SiO_{2-x}(OH)_x$ were separately dispersed in 10 ml ethanol by means of sonication for 30 min. The obtained dispersions were added to 20 g of epoxy resin and further sonicated for 30 min. Afterwards the mixture was poured in an aluminium pan, degassed under vacuum in an oven at 90 °C to remove entrapped air and solvents and finally cured for 3 h at 180 °C. According to this procedure, epoxy based nanocomposites containing 1 wt% of the four different fillers were prepared. The same degassing procedure and thermal curing cycle was adopted for the preparation the neat epoxy system.

2.7. Characterization

Fourier Transform Infrared (FT-IR) spectra of MWNT-COOHs, MWCNT-APTESs, and MWCNT-APTES-$SiO_{2-x}(OH)_x$ dispersed in KBr pellets were collected by using a Nicolet model 60SX FT-IR spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–400 cm^{-1}, 2 cm^{-1} spectral resolution and 32 scans. The filler powders were dried overnight at 110 °C before FT-IR data collection.

The morphology of MWNT-APTES and MWCNT-APTES-$SiO_{2-x}(OH)_x$ was investigated by TEM (JEM 100-CX instrument with an accelerating voltage of 20 kV) and by SEM (HITACHI X-650, Japan) microscopy. For TEM observations the multiwalled carbon nanotubes were dispersed in ethanol and dropped on a copper grid. For SEM observations the powders were sputter-coated with gold before observations.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB MKII (VG Scientific Ltd, UK) instrument, with an AlKa (14 kV, 350 W) excitation source and a 5-Channeltron detection system. Photoelectron spectra were collected at 20 eV constant pass energy of



Scheme 1. Illustration of (a) MWCNT-COOH, (b) MWCNT–APTES and (c) MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles.

the analyzer. The electron take-off angle was 45° with respect to the sample. Pressure during analysis was around 10^{-9} mbar. Functionalized MWCNTs were suspended in ethanol and deposited on a gold plate. The spectra were processed by the CasaXPS software by using a peak fitting routine with symmetrical Gauss–Lorentian function.

Thermo-gravimetric analysis (TGA) was carried out by using a Q5000 TA in order to investigate the effect of MWCNT functionalization as well as the thermal stability of epoxy based nanocomposites. The samples were heated from 25 °C to 800 °C at a heating rate of 10 °C/min under either air or nitrogen flows.

Optical microscopy was performed in transmission mode by using an Olympus BX51 in order to qualitatively investigate the particles size and homogeneity of the sample, i.e. nanotubes clusters size and their spatial distribution throughout the thickness of nanocomposite sample.

Nanocomposite specimens were tested under the single cantilever method by using a Dynamic-mechanical analyser (DMAQ800, TA Instruments) using an oscillation frequency of 1 Hz and a strain amplitude of 50 μm. The specimens were dried at 80 °C for 24 h before testing, and then tested from −20 °C to 300 °C at a heating rate of 3 °C/min.

Coefficients of thermal expansions, CTEs of epoxy nanocomposite were experimentally measured by thermal mechanical analysis (TMA) by using a Shimadzu TA60-WS machine equipped with a macro probe. The TMA scans were carried out on samples with square cross section (3 mm × 3 mm) and longitudinal length of 15 mm according to the ISO113598, with a 3 °C/min temperature ramp. For each scan, the sample was placed in the measurement cell and equilibrated at 30 °C for 10 min; linear dimension was monitored as the temperature increased to above the glass transition temperature.

Microcombustion calorimetry (MCC) measurements were carried out by using a FAA microcalorimeter instrument supplied by Fire Testing and Technology Ltd (UK) according to the ASTM D7309-07 standard. The heating rate was 1 °C/s and the maximum pyrolysis temperature was 700 °C with a combustion temperature of 900 °C. The flow was an O_2/N_2 mixture at a ratio of 20/80 cm^3/min and the sample weight was 5 ± 0.5 mg. The obtained values are the average of repetitions on three different samples.

3. Results and discussion

3.1. Characterization of functionalized and silica enriched MWCNTs

3.1.1. Chemical characterization

FTIR spectroscopy was used to investigate the extent of APTES functionalization of MWCNT-COOHs. FTIR spectra for MWCNT-COOH and MWCNT-APTES samples are reported in Fig. 2. The MWCNT-COOH spectrum reveals the

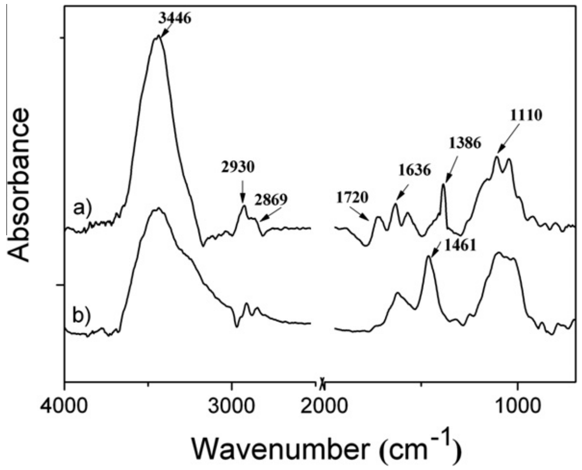


Fig. 2. FT-IR spectra of (a) oxidized multi-walled carbon nanotubes, MWCNT-COOHs and (b) multi-walled carbon nanotubes functionalized with 3-aminopropyltriethoxysilane, MWCNT-APTESs.

absorbance peak at around 1720 cm^{-1} assigned to the carbonyl group vibration of carboxylic acid groups alongside of the absorption bands at 2920 and 2860 cm^{-1} attributed to the CH stretching, the band at 1631 cm^{-1} assigned to conjugated C=C stretching, the band at 1567 cm^{-1} assigned to C=C stretching vibrations of the aromatic carbon in non-graphitic domains, the band at 1395 cm^{-1} due to the in-plane OH deformations vibrations of –COOH groups and the bands at 1097 and 1060 cm^{-1} assigned to C–O stretching vibrations [26].

The IR spectrum of the APTES functionalized MWCNT sample shows the disappearance of the band at 1720 cm^{-1} and the consequent appearance of the band at 1640 cm^{-1} which may be assigned to the amide carbonyl stretching vibration mode. The presence of new bands at 3100 and 1461 cm^{-1} corresponds to the stretching of N–H groups whereas the band at 1104 cm^{-1} can be attributed to the C–N bond stretching of the amide functional group [27]. The flattening of the absorbance bands in the region 1000–1200 cm^{-1} is ascribed to the presence of additional absorbance bands such as Si–O–R asymmetric stretching vibration and Si–C and Si–OH deformation vibrations which over impose to the MWCNTs bands [28]. This spectral evidence confirms the successful APTES functionalization of oxidized MWCNTs through the reaction of acidic groups with amine groups.

The FTIR spectrum of multi-walled carbon nanotubes enriched with silica nanoparticles (data not shown for brevity), MWCNT-APTES-$SiO_{2-x}(OH)_x$ reveals the prominent absorbance bands at 1090, 800 and 960 cm^{-1} ascribed respectively to the Si–O–Si stretching and bending modes and to the stretching of Si–OH groups of hydroxylated silica nanoparticles [28].

XPS results both as atomic compositions and high resolution spectra of N1s and O1s are reported, respectively in Table 1 and Fig. 3 for oxidized and APTES functionalized multi-walled carbon nanotubes. In particular Table 1 listed the atomic percentages of the elements which constitute the surface of the samples with the relative binding energy values (BE). The presence of both Si and N elements in the MWNT-APTES nanotubes and the concomitant reduction of carbon atoms with respect to MWCNT-COOH confirm the occurring of APTES functionalization. The small quantity of N (equal to 0.3 wt%) detected for the MWCNT-COOH sample, probably present as nitro or lactames groups, is due to the acid treatment [29].

The C1s high-resolution peak of the carbon nanotubes (spectrum not reported for brevity) was deconvoluted into five peaks at 284.5, 286.1, 288.6, 290.6, 292.5 eV. The main peak at 284.5 eV is attributed to the graphitic structure, whereas the other components, typical of the structure of the carbon nanotubes, are to be assigned to the presence of defects. In details the band at 286.1 eV is tentatively associated to carbon–carbon single bonds of defects on the nanotube structure (sp3) whereas the bands at 288.6 eV is attributed to C=O bonds in ketones and quinone, the band at 290.6 eV is ascribed to carbon atoms involved in C=O and O–C=O of carboxylic acid and esters groups, finally the peak at 292.5 eV may be ascribed to $\pi-\pi^*$ transition loss [30]. By comparing the atomic contents of the several carbon atoms it is shown that, due to the APTES functionalization, the intensity of peaks at high binding energy reduces. This confirms that the carbon nanotube surface has been chemically modified. The atomic percentage ratio of Si to C equal to 0.026 was found to be comparable to that (i.e. 0.0272) reported by Kathi et al. [31] for similar carbon nanotubes functionalization.

The emission band of O1s atoms for the MWCNT-COOH nanotubes was deconvoluted with three binding bands at 531.3, 532.9 and 535.6 eV assigned respectively to oxygen atoms double bonded to carbon in ketone and aldehyde moieties and oxygen atoms single bonded to carbon both from ether and hoxydryl groups (see Fig. 3(a)). The peak

Table 1
Summary of the surface atomic contents and core-level binding energy (BE) for MWNT-COOH and MWNT-APTES carbon nanotubes.

			C1s			N1s		O1s		Si2p
MWCNT-COOH										
BE (eV)	284.5	286.1	288.6	290.6	292.5	400.4	531.3	532.9	535.6	–
Atomic %	56.2	23	7.2	4.3	1.3	0.3	3.7	3.6	0.5	–
Total %			91.9			0.3		7.8		–
MWCNT-APTES										
BE (eV)	284.5	286.1	288.6	290.6	292.5	400.4	531.1	532.8	–	102.6
Atomic %	53.5	21.7	5.9	2.5	0.5	4.6	2.7	5.6	–	2.2
Total %			84.1			4.6		9.1		2.2

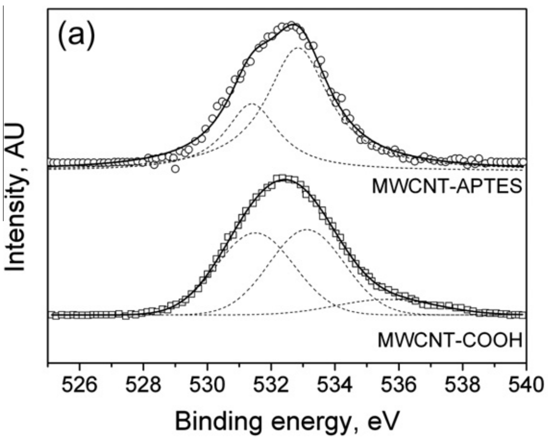


Fig. 3. X-ray photoelectron spectroscopy of (a) O1s spectra of MWCNT-COOHs and MWCNT-APTESs and (b) N1s spectra of MWCNT-APTESs and neat 3-amminopropyltriethoxysilane (APTES).

at 535.6 eV is commonly assigned to adsorbed water molecules. Moreover, since oxygen atoms in esters and carboxyls groups have both single and double bonds, they contribute to the aforementioned component peaks. After functionalization with APTES the emission band of O1s is deconvoluted by using only two chemical binding bands at 531.1 and 532.6 eV. The significant intensity increment of the band at 532.8 eV observed for the MWCNT-APTES sample is to be ascribed to the presence of oxygen atoms bonded to silicon and carbon atoms –C–O–Si– of silanes [32] likely due to the alkoxy groups.

In Fig. 3(b) the reference APTES shows an emission band for N1s which can be deconvoluted with two peaks at 399.6 and 401.5 eV assigned respectively to ammine and ammonium nitrogen atoms. Whereas, the line shape analysis of N1s for the sample MWCNT-APTES allows to identify only one band corresponding to nitrogen atoms with binding energy equal to 400.4 eV. This XPS result may be ascribed to the formation of amide groups from reaction of amine silanes with carbossilic acid groups located on the carbon nanotubes surface with no evidence of interactions through silanol groups or amine acid–basic interactions [33].

3.1.2. Thermal characterization

TGA curves collected under air flow for unmodified, ammino functionalized and silica enriched carbon nanotubes are reported in Fig. 4.

Due to the differences in the thermal stability of the carbon nanotube structure and the acidic or silane anchored moieties, by TGA analysis it is possible to gain a reliable estimation of the relative amount of introduced functionalities. The weight loss difference between 250 and 450 °C is about 12 wt% for MWCNT-COOHs and about 7 wt% for MWCNT-APTESs compared to the negligible loss exhibited by the neat MWCNTs. These data confirm that both acid functionalization and amine grafting reactions have taken place. The weight loss of about 12 wt% detected at 220 °C for the MWCNT-APTES sample is tentatively ascribed to the removal by volatilization of absorbed DMF solvent. The presence of APTES moieties along with silica nanoparticles anchored on the carbon nanotubes increases the temperature ascribed to the maximum degradation of the graphitic skeleton of nanotubes of about 80 °C (i.e. from 580 °C for MWCNT to 660 °C for MWCNT-APTES and MWCNT-APTES-$SiO_{2-x}(OH)_x$ system). Furthermore from the residues at 750 °C it is possible to estimate the content of silica nanoparticles, as SiO_2 equivalent content, present in the sample MWCNT-APTES-$SiO_{2-x}(OH)_x$ to be equal to approximately 70 wt%.

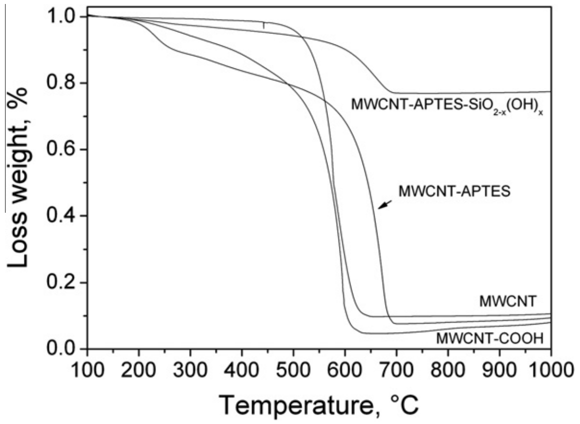


Fig. 4. TGA curves of pristine and differently functionalized MWCNTs.

3.1.3. Morphology of functionalized MWCNTs

The surface morphology of functionalized MWCNTs was observed by means of SEM and TEM analysis. Fig. 5 shows the SEM images of MWNT-APTES and MWCNT-APTES-$SiO_{2-x}(OH)_x$. The carbon nanotubes are well distinguishable in the sample MWCNT-APTES whereas the silica particles resulted attached on the surface of the functionalized MWNT-APTES and partially aggregated in the sample MWCNT-APTES-$SiO_{2-x}(OH)_x$. This is also shown by TEM images.

As shown in Fig. 6(a) the average diameter of the functionalized MWNT-APTES is about 10–15 nm, according to

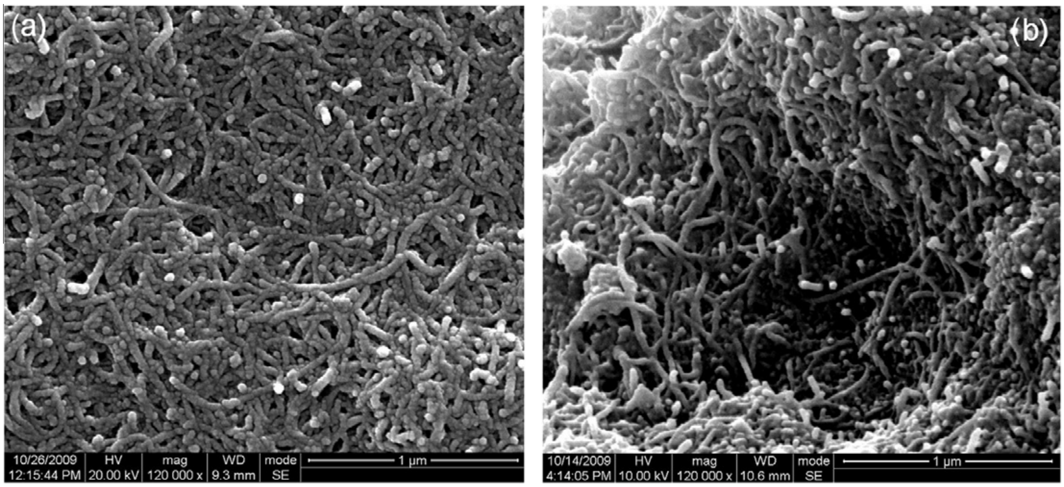


Fig. 5. SEM images of (a) MWNT-APTES and (b) MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles.

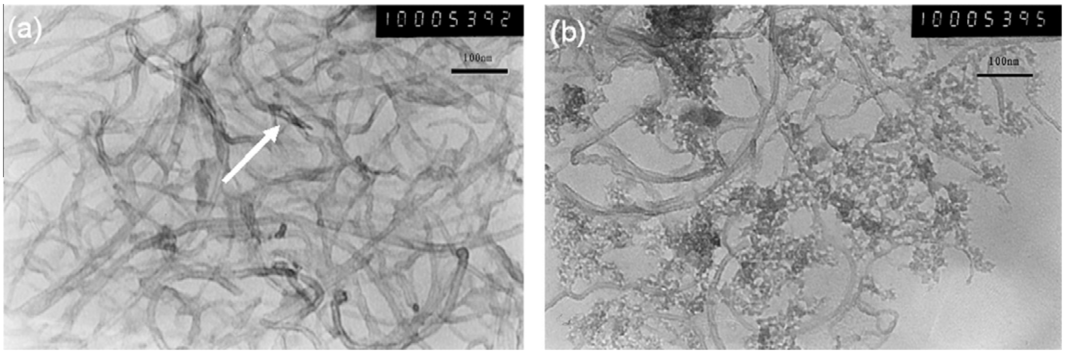


Fig. 6. TEM photographs of (a) MWNT-APTES and (b) MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles.

the nominal diameter of neat carbon nanotubes. The morphology of MWCNT after functionalization appears to remain intact. Some amorphous materials (pointed by the white arrow in Fig. 6(a) attached to the surface of the silanized MWCNTs are supposed to be derived from the APTES silane molecules [31]. Fig. 6(b) shows that the silica particles prepared by Stöber method have a diameter of ~10 nm and that they are aggregated to form some "bunches" attached on the surface or at the ends of the functionalized MWNT-APTESs.

3.2. Characterization of epoxy based nanocomposites

3.2.1. Morphological characterization and thermo-mechanical properties

Optical micrographs reveal that the texture distribution of nanofillers within the epoxy matrix depends on the different surface functionalization. Epoxy nanocomposites with MWCNT-COOHs (see Fig. 7(a)) present solid-like spot formation all over the sample with compact morphology indicating that the dispersion procedure had no effect below certain dimension (average aggregate dimension around 50–70 µm). In the case of nanocomposites filled with MWCNT-APTES (Fig. 7(b)) and MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles (Fig. 7(c)) a better dispersion can be appreciated on microscale range. Smaller average aggregates are visible by optical microscopy with surrounding bigger aggregate very shadow area which lead to assume that pristine aggregate was debundled at lower size level. In these two latter cases, the average sizes of micro-sized formation were evaluated within the range 5–10 µm. This result confirms that the silanization of CNTs alongside the presence of silica nanoparticles aggregate as "bunches" morphology allow a more homogeneous dispersion of the carbon nanotubes throughout the samples volume [34].

The effect of surface MWCNT functionalization on the temperature-dependent mechanical properties of nanocomposites was investigated by DMA analysis by comparing the storage modulus, loss modulus and tanδ values with those of neat epoxy. Typical DMA curves for neat epoxy and composite systems are shown in Fig. 8(a) and (b).

The storage modulus depends on the functionalization of MWCNTs and gradually increases in the order Epoxy < nanocomposite filled with MWCNT-COOH < nanocomposite filled with MWCNT-APTESs < nanocomposite filled with MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles. At

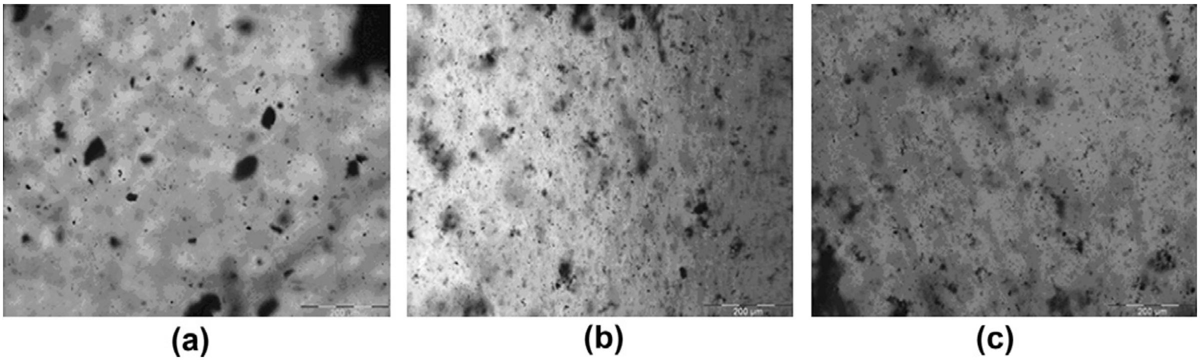


Fig. 7. Optical micrographs at 10× magnification, (a) epoxy nanocomposite with MWCNT-COOHs; (b) epoxy nanocomposite with MWCNT-APTESs; (c) epoxy nanocomposite with MWCNT-APTES-SiO$_{2-x}$(OH)$_x$s.

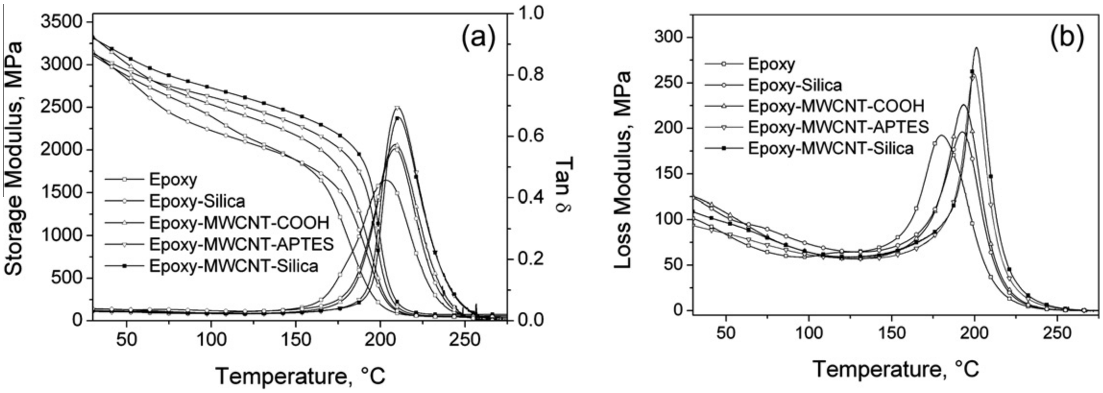


Fig. 8. Storage modulus and tanδ (a) and Loss modulus (b) of neat epoxy and composite materials.

120 °C, which represents the maximum service temperature for neat epoxy (i.e. approximately equal to the T_g reduced of 80–90 °C), the storage modulus of neat epoxy is 2.1 GPa while it is equal to 2.4, 2.5 and 2.6 GPa, respectively for the composites containing 1 wt% of MWCNT-COOH, MWCNT-APTES and MWCNT-APTES-SiO$_{2-x}$(OH)$_x$ particles. On the other side the storage modulus of the epoxy nanocomposite containing 1 wt% of Stober silica nanoparticles is, in the range of investigated temperature, somewhat comparable with the modulus of neat epoxy (i.e. at 120 °C it is equal to 2 MPa). At 190 °C the storage modulus is 486 MPa for neat epoxy and 1137, 1632 and 1867 MPa, respectively for epoxy based composite filled with MWCNT-COOH, MWCNT-APTES and MWCNT-APTES-SiO$_{2-x}$(OH)$_x$ particles. Thus the sample containing 1 wt% of multiwalled carbon nanotubes enriched with silica nanoparticles exhibits at 120 °C and 190 °C a storage modulus increased by about 25% and 280% with respect to neat epoxy system. The improvement of glassy and rubbery moduli observed for the samples containing functionalized MWCNTs may be attributed to both the better interfacial interactions between the functionalized MWCNTs and epoxy matrix [35,36] and the effect of silane functionalization and silica nanoparticles which contribute to enhance the CNTs dispersion [24]. In details MWCNT-COOHs present a hydrophilic surface which is compatible with the network of the cured epoxy resin whereas MWCNT-APTESs present ethoxy groups (–SiOEt) which may potentially react with hydroxyl groups of the epoxy cross-linked network. As for the MWCNT-APTES-SiO$_{2-x}$(OH)$_x$ particles, the surface hydroxylated silica nanoparticles contribute to improve both the compatibility of the filler with the epoxy network and the dispersion of carbon nanotubes which are mechanically more effective than silica particle in transferring the load. In this view the silica nanoparticles cooperate synergistically with the functionalized MWCNTs in the enhancement of the mechanical properties of the resulting composite materials.

Fig. 8(a) shows the tanδ, equal to the ratio of loss modulus to the storage modulus, as a function of the temperature for neat epoxy and composite materials. The composite materials display tanδ curves narrower than that of neat epoxy resin. This is due to the effect of surface fuctionalization of the carbon nanotubes which, exhibiting an improved interfacial strength with the epoxy matrix, effectively discourage the macromolecules relaxations activated by temperature. However the composites exhibit tanδ values at maximum significantly higher than neat epoxy resin as due to the significant increase of Loss modulus (see Fig. 8(b)). This result confirms that at the tested frequency of 1 Hz, the functionalized and silica decorated

MWCNTs in the epoxy matrix promote a greater energy dissipation (i.e. dumping effect) likely through a mechanism involving carbon–carbon nanotubes sliding and relaxations within the inorganic silica "bunches" morphology [24].

The glass transition temperature of composite materials, determined from the maximum peak of the loss modulus, increases with respect to the neat epoxy by 13, 19 and 22 °C with the addition of 1 wt% of MWCNT-COOHs, MWCNT-APTESs and MWCNT-APTES-$SiO_{2-x}(OH)_x$s respectively. This occurs because the functionalized MWCNTs, mainly those functionalized with APTES and enriched with silica nanoparticles, are better dispersed within the epoxy matrix producing a network which hinders the relaxation of epoxy macromolecules [37]. However along side with the physical effect of carbon nanotubes it is also worth considering that some reactive groups present in the silica enriched nanotubes such as SiOH groups may catalyze the epoxy crosslinking reactions and give arise to an epoxy network with enhanced thermal-mechanical properties [38].

Neat epoxy and nanocomposite samples were scanned by thermo-mechanical analyzer (TMA) to evaluate the coefficient of thermal expansion, CTE in both rubber and glassy regions.

The CTE mismatch between matrix and fibers is among the main controlling factors for the arising of residual stresses within composite materials. In this respect, TMA data provide fundamental information of the effect of the nanoparticles on the expansion behavior of the resin matrix for a temperature change under and above glass transition.

For each composite the dimension change curves and the CTE values are reported respectively in Fig. 9(a) and (b). CTE values under and above T_g were calculated by the slope of the linear regression line within the glassy and rubber region. It was found that CTE of the system does not change significantly compared with the neat epoxy. However, according to literature [39,40], the glassy CTE values for composites loaded with MWCNT-COOHs show a 8% decrease with respect to neat epoxy resin, whereas for the rubbery CTE a variation equal to 10% and 5% respectively for MWNT-APTES and MWCNT-APTES-$SiO_{2-x}(OH)_x$ particles was measured.

3.2.2. Thermal properties and flammability

The composites filled with 1 wt% of functionalized and silica decorated MWCNTs have been tested for thermal stability by TGA analysis in nitrogen atmosphere and for flammability behavior by micro-combustion cone calorimeter.

Owing that the functionalized and the silica enriched multiwalled carbon nanotubes are better dispersed within the epoxy matrix compared with the acid functionalized nanotubes, the initial decomposition temperatures at 5 wt% (T_5) and 10 wt% (T_{10}) weight loss and at the maximum decomposition rate (T_{dm}) slightly increase with respect to the neat epoxy resin (see Table 2).

Temperature increment of only few degrees (i.e. 4–7 °C) could be reasonable attributed to the physical barrier effect for the presence of functionalized and silica enriched MWCNTs which hinders the propagation of degradation reactions [24,41].

Microscale combustion calorimeter (MCC), developed by FAA researchers [42], represents a valid scientific technique to measure flammability property of material. This technique separates the solid state and gaseous phase evolving from a flaming combustion followed by a completely combust in excess of oxygen. The microcalorimeter technique (also called Pyrolysis-combustion flow calorimetry) is a verified method for measuring static (HRC—Heat Release Capacity and THR—Total Heat Release) and dynamic (HRR—Heat Release Rate) combustion parameters of materials.

The HRR value represents the rate of released heat by microgram-size sample while the HRC, which represents a novel indicator of material flammability hazard, identifies the "tendency" of the system to release heat under fire conditions. This later value can be correlated by empirical model or physical based calculation with fire indicator and with good approximation it may indicate the average flaming heat release rate of the considered system. HRC can be also considered to formulate self extinguishing criterion based on UL94 and LOI flammability test as reported in [43] for a wide series of pure polymers. Neat epoxy and

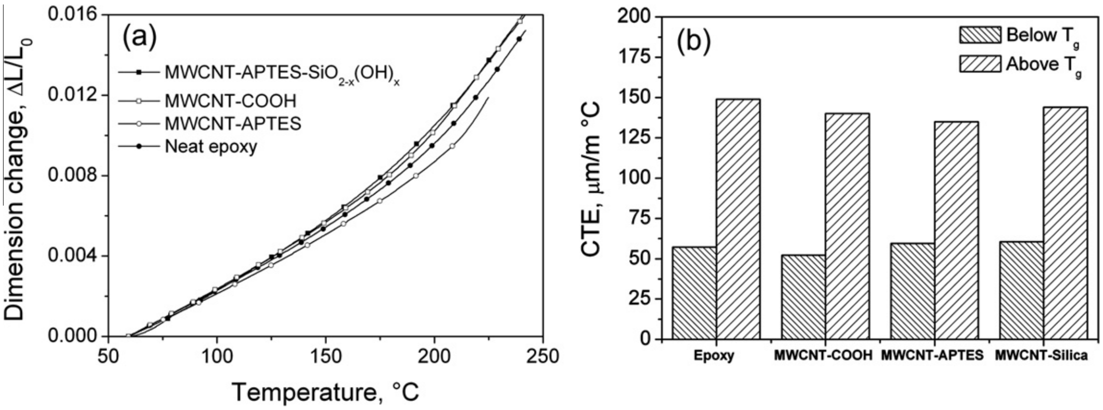


Fig. 9. Dimension change curves (a) and coefficient of thermal expansion (b) for neat epoxy and composites filled with functionalized and silica enriched carbon nanotubes.

Table 2
Thermal and flammability parameters for neat epoxy and composite with functionalized and silica enriched carbon nanotubes.

Sample	T_5 (°C)	T_{10} (°C)	T_{dm} (°C)	Residual yield at 800 °C (wt%)	THR (kJ/g)	HRC (J/gK)
Epoxy	357	373	380/400	21.6	17.4 ± 0.5	660 ± 50
Nanocomposite with MWCNT-COOH	356	374	380/396	25.6	18.1 ± 0.5	597 ± 20
Nanocomposite with MWCNT-APTES	364	377	380/402	23.6	17.3 ± 0.5	801 ± 50
Nanocomposite with MWCNT-$SiO_{2-x}(OH)_x$	364	377	380/400	23.4	16.9 ± 0.5	604 ± 50

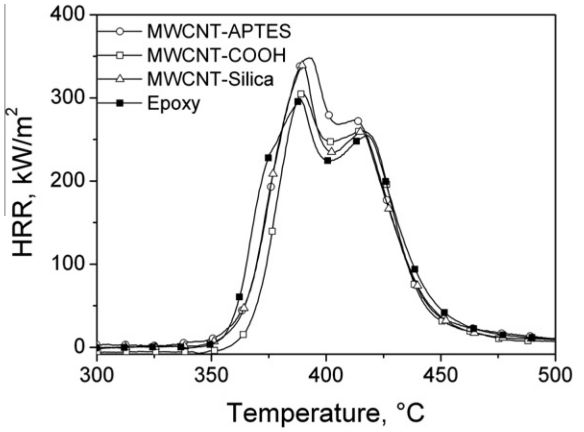


Fig. 10. Averaged HRR curves for neat epoxy and epoxy nanocomposites loaded with functionalized and silica enriched carbon nanotubes.

epoxy nanocomposite filled with functionalized carbon nanotubes were tested by MCC and HRR curves are reported in Fig. 10.

Results show that time to ignition does not change significantly by adding the functionalized or silica decorated MWCNTs and the initial flammability temperature of all the system fall within the narrow range of 340–350 °C. A slight variation of the shape of the HRR curves for loaded systems results if compared with neat epoxy curve mainly during the first stage (see range from 350 °C to 400 °C). The maximum decomposition temperatures are in accordance with corresponding values by thermo-gravimetrical analysis and they fall within the range from 385 °C to 395 °C.

The THR changes slightly in the case of silica enriched MWCNTs of about 5% compared with neat system, whereas it remains substantially constant for MWCNT-APTESs loaded epoxy (see Table 2). It is also convenient to note that when MWCNT-COOHs are filling the epoxy system the THR value increases of about 5%. Interesting results are reported for the specific heat released (HRC). In fact, significant variation is shown for the epoxy system loaded with APTES-MWCNTs which shows a positive change of more than 20%; whereas a decreased value (10% less) is recorded for the same parameter in the case of epoxy naocomposite filled with MWCNT-COOHs and silica enriched MWCNTs. The found values for the HRC and THR are in accordance with previously published data on similar resin [44,45].

4. Conclusion

In the present work the effects of both APTES functionalized and silica enriched MWCNTs on the thermo-mechanical and thermal properties of epoxy composites have been investigated. The silanization of multi-walled CNTs is obtained by reacting the amino groups of APTES with the acidic groups generated sidewalls by oxidation of CNTs. Afterwards the silane functionalized CNTs have been modified with preformed silica nanoparticles, obtaining silica enriched carbon nanotubes with the "bunches" morphology. Results have shown that APTES functionalized and silica enriched carbon nanotubes are better dispersed within the epoxy matrix exhibiting smaller aggregate compared with acid functionalized MWCNTs. Moreover, it has been proven that composites containing functionalized and silica enriched MWCNTs exhibit better thermal-mechanical properties in terms of higher storage modulus, higher T_g and improved dumping behavior in comparison to neat epoxy resin. In particular silica nanoparticles and functionalized carbon nanotubes act synergistically to improve the filler dispersion and enhance the storage modulus of epoxy nanocomposite of about 25% in the glassy region and 280% in the rubbery region with respect to neat epoxy.

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