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Multiwalled carbon nanotubes functionalized with 7-octenyltrichlorosilane and *n*-octyltrichlorosilane: dispersion in Sylgard®184 silicone and Young's modulus

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Abstract Sylgard®184/multiwalled carbon nanotube (MWNT) composites have been prepared by in situ polymerization using purified and functionalized multiwalled carbon nanotubes (f-MWNTs) as fillers. Surface modification of the MWNTs has been carried out by silanization with 7-octenyltrichlorosilane (7OTCS) and *n*-octyltrichlorosilane (*n*OTCS). The modification and dispersion of the carbon nanotubes in composites were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron spectroscopy (TEM), and high-resolution transmission electron spectroscopy (HRTEM). Young's modulus results were derived from indentation testing. It is shown that the terminal-vinyl group of 7OTCS molecules plays an essential role for both the dispersion of the f-MWNTs in the composite and its mechanical properties. At loading as low as 0.2 wt%, the Young's modulus is shown to increase up to 50%. This is interpreted as resulting from a combination of the good compatibility in the forming silicone matrix of the MWNTs coated with a siloxane network, on the one hand, and the covalent links created between the terminal-vinyl groups and the host matrix in formation, on the other hand.

Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been the subject of an impressive number of investigations owing to their exceptional chemical and physical properties: density, strength, modulus, electrical, and thermal conductivities. Among applications showing definite potential is their use as superior fillers in polymer matrices with the prospect of greatly improving the mechanical, electrical, and thermal properties of the resultant materials [2–5].

Silicone-based materials, which are chemically stable, resistant to UV radiation, and electrically insulating, are extensively used in automotive, textile, and aerospace industries as protective coatings, sealants, lubricants, resins, etc. There is a growing interest in preparing silicone/CNT composites where CNTs could advantageously replace other fillers such as silica and carbon black [6], in a variety of applications such as highly and reversibly deformable rubbers, heat-dissipating materials, infrared actuators, flexible field-emission devices, flame retardants, and highly insulating silicone composites, to cite a few [6–11].

Sylgard®184, the host matrix of interest in this study, is a thermally curable silicone rubber. Its formulation consists of two parts: vinyl-terminated PDMS chains (part A) and a mixture of methylhydrosiloxane copolymer chains with a

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Pt catalyst and an inhibitor (part B). Parts A and B are viscous liquids, 5000 and 110 cSt (at 25 °C), respectively, usually mixed together in a 10:1 ratio. Addition of a catalytic amount of the SiH of methylhydrosiloxane (part B) to the double bond of the vinyl-terminated PDMS species (part A) leads to a cross-linked network through the formation of Si–C covalent bonds. Sylgard®184/CNT composite elaboration in bulk involves a solution processing which requires good dispersion of the CNTs [12]. In addition, reinforcement properties in polymer/CNT composites require optimal transfer of strain between components in the composite, which implies the formation of robust interfacial bonding between CNTs and the host matrix [5]. A way to achieve this goal is to cause the CNTs form chemical bonds during the curing step and have them covalently integrated in the cross-linked matrix. In this general context, forming adherent Sylgard®184/CNT composites on aluminum substrates is of special interest for aerospace industry owing to the superior flame-retardant properties such materials have already shown.

Recently, we have proposed an approach to form Sylgard®184/multiwalled carbon nanotube (MWNT) composite where both dispersion and Si–C bond formation are promoted during the cross-linking phase of the composite [13]. First, MWNTs were functionalized called functionalized MWNTs (f-MWNTs) with an organosilane molecule, 7-octenyltrichlorosilane. The use of silanes was motivated by the fact that at the same time as they graft on the MWNTs they also form siloxane networks on the CNT surface through condensation with neighboring silane molecules. The similarity in chemical nature of the siloxane network on the f-MWNTs and the PDMS chains in parts A and B is propitious to their dispersion in the fluids, and hopefully in the composite. To help the dispersion further, the f-MWNTs were mixed in the predominant more viscous component (part A) containing the vinyl-terminated PDMS species. Accordingly, the silane-coupling molecules are chosen to bear vinyl-terminal groups to form Si–C bonds when mixed with the species bringing the complementary reactive Si–H functions (part B). The three-partner reaction is schematized in Fig. 1. In a previous contribution [13], we were not in a position to observe the surface morphology of the f-MWNTs, their dispersion in the composite nor to assess mechanical properties.

The purpose of this investigation is to compare the dispersion of f-MWNTs in Sylgard®184/MWNT composites and the resulting enhancement of the Young's modulus induced by two analogous silane molecules differing only by the nature of their end groups, 7-octenyltrichlorosilane, $CH_2{=}CH{-}(CH_2)_6{-}SiCl_3$ or 7OTCS, and *n*-octyltrichlorosilane, $CH_3CH_2{-}(CH_2)_6{-}SiCl_3$ or *n*OTCS, respectively (Fig. 2). Through this comparison, it is shown that the terminal-vinyl group in 7OTCS is essential for both the dispersion in the composite and its mechanical properties.

Experimental

Chemicals

7-Octenyltrichlorosilane (95%, ABCR, SIO6708.0) and *n*-octyltrichlorosilane (97%, ABCR, AB111290) used as silane-functionalization agents were stored in sealed recipient vial under argon atmosphere. As in our previous studies [13–16], trichlorosilanes have been preferred to trialkoxysilanes [17–19] because of the higher reactivity of the formers. The following reagents needed in the purification, oxidation, reduction, and functionalization steps of the MWNTs were purchased from Acros Organics and used as received: sodium hydroxide (50 wt% solution in water, 1310-73-2), sulfuric acid (96.00%, 766493-9), nitric acid (63%, 7697-37-2), and diisobutylaluminum hydride

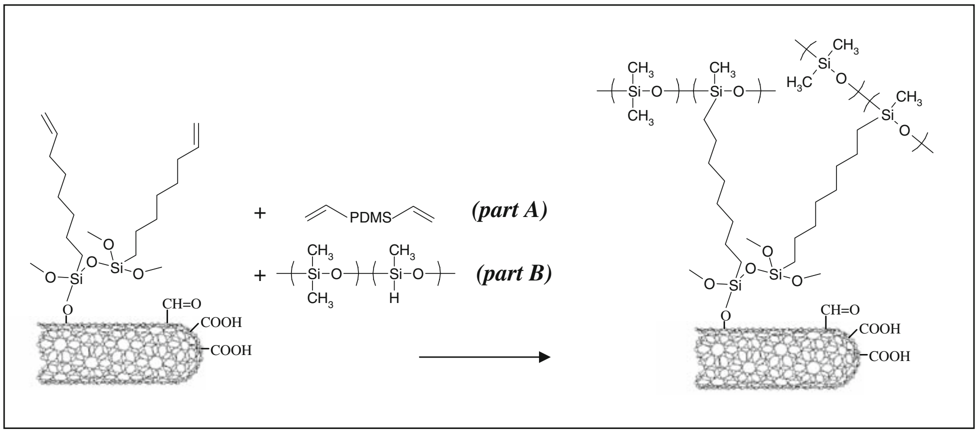

Fig. 1 Scheme of the reaction of f-MWNTs with 7-octenyltrichlorosilane with silicone elastomer (part A and B) for the preparation of MWNTs/silicone composite

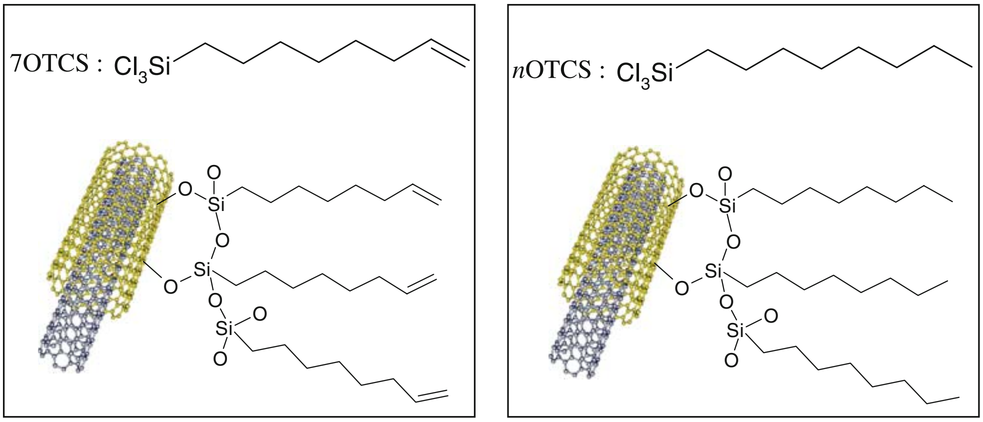

Fig. 2 Molecular structure of 7-octenyltrichlorosilane and *n*-octyltrichlorosilane and their schematized grafting on a MWNT

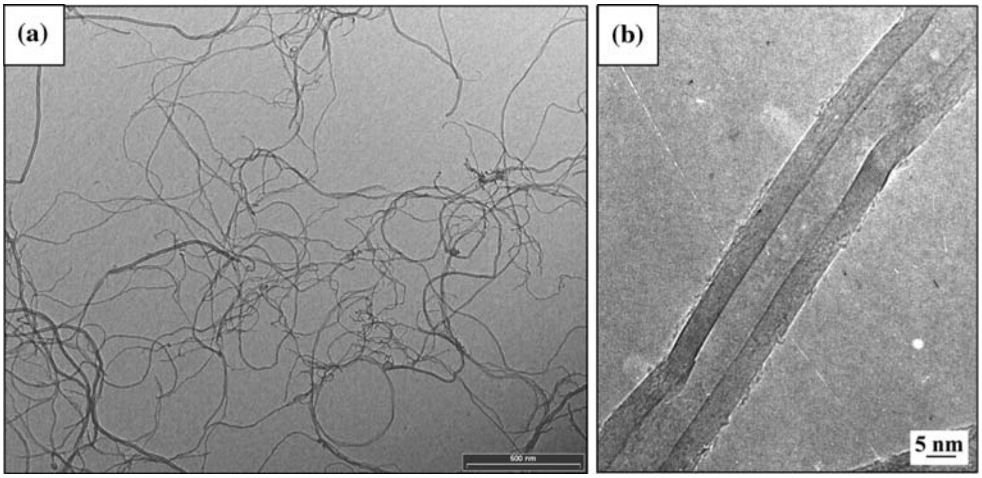

Fig. 3 **a** TEM and **b** HRTEM pictures of raw MWNTs

[DIBAL-H] (20 wt% solution in toluene, 1191-15-7). Ethyl alcohol (denaturated with up to 5% ether, Disinfectol®, Chem Lab, 64-17-5), absolute ethanol pro-analysis (Merck, 1.00983.2500) and water, obtained from a Milli-Q Plus ultra-pure Millipore 6.0 water system (18 MΩ cm). Toluene HPLC grade (Lab-Scan, C22C11X) and triethylamine (99+%, Aldrich, 23,962-3) were dried by distillation on phosphorus pentoxide (97%, Aldrich, 21,470-1) and stored under argon atmosphere.

Nanotubes synthesis and purification

The MWNTs used in this study were produced directly in the laboratory by catalytic decomposition (CCVD) of ethylene on a cobalt/iron catalyst supported on alumina following a procedure described elsewhere [20]. The as-obtained black powder contains MWNTs, metallic catalytic particles, and alumina. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements indicate that the raw MWNTs have an external diameter of 13 ± 5 nm, an internal diameter of 5 ± 2 nm, a length of the order of 10 μm, and a thin layer of amorphous carbon on the sidewalls of the CNT (Fig. 3a, b).

Functionalization of the MWNTs

The MWNTs have been functionalized with 7OTCS and *n*OTCS following a procedure which comprises four steps: purification of the MWNTs in NaOH to eliminate the catalytic support, their oxidation in a HNO_3/H_2SO_4 mixture, followed by a reduction of the ketone and carboxylic functions into –OH groups with diisobutylaluminum hydride, and functionalization with the organotrichlorosilanes [13, 14]. The reduction step of ketones and carboxylic groups is motivated by the specific reactivity of the trichlorosilanes with –OH functions.

Composites preparation

Composites of Sylgard®184/MWNTs were prepared by mechanical mixing f-MWNTs (0.01, 0.10, 0.20, and 0.50 wt%) with part A at 6000 rpm during 30 min, in a

5 cm^3 cylindrical container and at a temperature kept at 25 °C. Parts A and B were then added to the blend in a ratio 10:1. The composites were cured during 2 h at 100 °C [13]. The dimensions of the composites films produced are 200 mm × 20 mm × 3 mm (thickness).

Characterization

Thermogravimetric analyses (TGA, Netzsch STA 409 PG) on MWNT samples of about 10 mg are carried out in a helium atmosphere (100%) for temperatures ranging from 25 to 1200 °C at a heating rate of 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) analyses were conducted on f-MWNTs to evaluate quantitatively and qualitatively their chemical composition. Photoelectron spectra were measured with a HP 5950A using the monochromatized Al Kα radiation (1486.6 eV). The analyzed core-level lines (C 1s, O 1s, Si 2p, Al 2p) are calibrated with respect to the C 1s binding energy set at 284.6 eV corresponding to the sp^2 hybridized carbons largely present in the aromatic CNT structure.

The dispersion of MWNTs in silicone composite is assessed by TEM (Philips Tecnaï T10) after cutting slices with thickness of 60 nm by cryo-ultramicrotomy and deposited on conventional TEM grids. An average of 10 slices is analyzed for each composite containing different CNT loadings. The morphology of CNTs was checked by HRTEM (JEOL 200CX). The samples of MWNTs are ultrasonically dispersed in absolute ethanol and a drop of the solution is deposited on carbonated Formvar® microscopy grids.

The mechanical properties of CNTs/silicone composites have been investigated with indentation testing, a semi-destructive mechanical characterization at the microscopic scale, carried out on the surface of the nanocomposite. These properties are obtained by measuring the continuous resistance to the penetration in the material of an indenter (steel spherical tip, Ø = 10 mm) while simultaneous load and displacement are recorded. The local Young's modulus (E^*) is derived from the following expression:

$$E^* = \frac{3}{4}\frac{F}{\delta^{3/2}R^{1/2}}$$

where F is the maximum loading (N) obtained during the indentation, δ the depth of the indentation (m), and R the radius of the spherical tip (m). E_{sample}, the Young's modulus of the sample, is extracted from the equation below,

$$\frac{1}{E^*} = \frac{1-\nu_{\mathrm{ind}}^2}{E_{\mathrm{ind}}} + \frac{1-\nu_{\mathrm{sample}}^2}{E_{\mathrm{sample}}}$$

which contains the mechanical characteristics of the indenter (Poisson ratio $\nu_{\mathrm{ind}} = 0.30$, $E_{\mathrm{ind}} = 210\ 000$ MPa) and the estimated sample Poisson ratio ($\nu_{\mathrm{sample}} = 0.50$) assumed to be an incompressible material.

Results and discussion

f-MWNTs (7OTCS and *n*OTCS)

The f-MWNTs functionalized with *n*OTCS have been characterized by XPS, TGA, TEM, and HRTEM. Results obtained are generally comparable to those on 7OTCS, which is not surprising owing to the very analogous nature of their hydrocarbon chains (Fig. 2) [13].

The XPS survey spectra and the Si 2p line have been recorded on f-MWNTs functionalized with *n*OTCS to check the extent of the functionalization and compare it with what had already been observed on 7OTCS [13]. Qualitatively and quantitatively, the XPS results on *n*OTCS (not shown here) are essentially similar to those obtained with the closely related 7OTCS molecule. Of particular relevance is the fact that structure of the Si 2p line is indicative of the presence of a siloxane network at the surface of the f-MWNTs functionalized with *n*OTCS, which confirms our previous results on 7OTCS, $N{\equiv}C(CH_2)_3SiCl_3$, and $CF_3(CF_2)_5(CH_2)_2SiCl_3$ grafted on MWNTs [13–16], and those reported by Ma et al. in the case of a functionalization of MWNTs with an alkoxysilane [18].

TGA measurements (not shown here) point to a thermal stability of the CNT–O–Si links up to 250 °C, i.e., close to the value (225 °C) previously obtained for 7OTCS [13].

TEM analysis (not shown here) on *n*OTCS and 7OTCS leads to conclusions similar to those made in a previous study on the silanization of MWNTs, both with alkoxy- and chlorosilanes, namely, that the layered structure of the MWNTs after functionalization remains apparently unharmed, and that their external average diameter is maintained (8–15 nm) [13–19]. This is further confirmed by representative HRTEM images of f-MWNTs functionalized with 7OTCS (Fig. 4a–c). The presence of a mostly continuous siloxane network is distinctively perceived on top of the layered carbon structure of the f-MWNTs. On closer inspection, it appears that the average thickness of this siloxane film is of the order of 2–3 nm (Fig. 4c). Equivalent results are obtained for *n*OTCS.

Dispersion of the f-MWNTs in the composites

Before considering the dispersion of the f-MWNTs in the composite, it is worthwhile to begin with their behavior in the silicone base (part A). Reflected light microscopy measurements made on MWNTs functionalized with 7OTCS and mixed in the silicone base (part A) pointed out

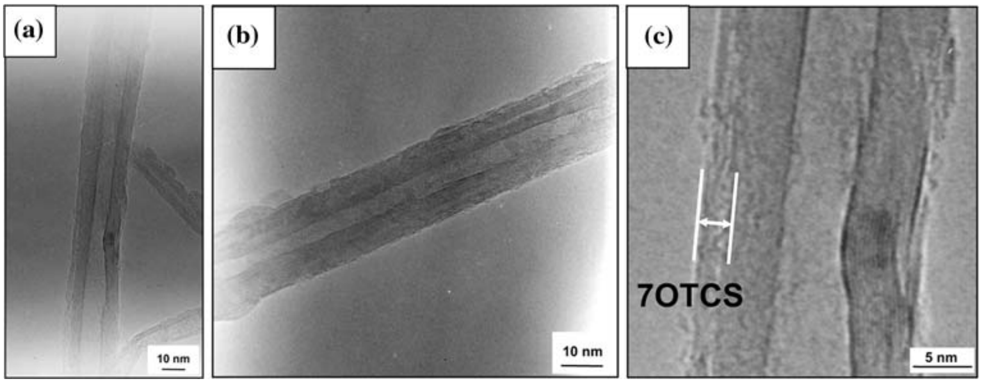

Fig. 4 HRTEM pictures (**a** and **b**) of MWNTs functionalized with 7-octenyltrichlorosilane. Functionalized CNTs wrapped with a 7OTCS-based siloxane layer (**c**)

to a significantly improved dispersion over the purified and reduced MWNTs [13]. Experiments have been carried out on f-MWNTs functionalized with *n*OTCS and similar results were found, in all probability, attributable to the compatibility of the siloxane network at the surface of the f-MWNTs with the PDMS chains in the silicone base.

For the benefit of the forthcoming discussion, it is useful to begin with the dispersion of purified MWNTs (0.5 wt%) into the Sylgard$^{®}$184 composite formed according to the protocol described in the Experimental section. The TEM image (Fig. 5a) shows not only individual MWNTs, but also several aggregates of CNTs pointing out to an overall imperfect dispersion. The occurrence of the individual nanotubes might result from a shearing-assisted debundling induced during the mechanical mixing of f-MWNTs in part A (6000 rpm, 30 min). In addition to the formation of the Si–C covalent bonds mainly leading to the cross-linked network (Fig. 1), other reactions can contribute to increase the cross-linking density of the rubber and indirectly to the dispersion of the CNTs. During the blending and the cross-linking phases, the Si–H functions on the methylhydrosiloxane copolymers present in part B can react with the carboxylic acids, ketone, and –OH groups present on the surface of the purified MWNTs and form C–O–Si links. Furthermore, some alkoxysilane groups can be converted in silanol groups which then can react with other Si–H function yielding Si–O–Si bonds. These reactions are known to be catalyzed by the hydrosilylation catalyst used in the formulation of the Sylgard$^{®}$184 silicone.

When f-MWNTs (0.5 wt%) modified with 7OTCS are used (Fig. 6b, c), the dispersion appears to be clearly more uniform than in the case of the composites formed with the purified MWNTs. In particular, very few small aggregates are found. At first glance, this could be interpreted as the result of the already pointed out compatibility induced by the siloxane network coating the surface of the f-MWNTs. However, when the f-MWNTs modified with *n*OTCS (0.5 wt%) are used to form a composite and, nevertheless, due to the fact that they disperse well in part A (such as 7OTCS-based f-MWNTs), essentially no individual f-MWNT could be observed. The experiments have been carried out several times and, in spite of repeated efforts to identify individual f-MWNTs in the TEM images of the many composites formed, only very big aggregates could be identified, a representative of which is shown in Fig. 5d. Thus, the divergent behavior noted between the MWNTs functionalized 7OTCS and *n*OTCS points to the very important role played by the reactive terminal-vinyl groups on the ultimate dispersion of the CNTs in the composite. In a recent study on ultra-thin layers of 7-octenyltrimethoxysilane and *n*-octyltrimethoxysilane grafted on an Al 2024 alloy substrate, the critical role of the terminal-vinyl function on the adhesion of Sylgard$^{®}$184 films to the substrate has been evidenced [21]. Adhesion results from the formation of interfacial Si–C bonds between the ultrathin layer of 7-octenyltrimethoxysilane coupling molecules and the overlaying silicone rubber. This supports the fact that the absence of suitably reactive functions on their surface leaves the MWNTs functionalized with *n*OTCS as spectators during the cross-linking process. The net result is their likely exclusion from the zones where Si–C bonds are formed with the unfortunate result that they re-aggregate, which is detrimental to the mechanical properties, as seen below. The intermediate dispersion observed in the case of composites based on the modified MWNTs bearing various chemical functionalities (–COOH, >CO, –OH, …) is consistent with this picture that reactive functions on the CNTs play an important role on their dispersion in the host matrix. In the sequel, this is considered in terms of the Young's modulus.

Young's modulus of the composites

In all the experiments, a maximum load of 0.2 N corresponding to a tip penetration of 10 μm has been applied; the thickness of the samples subject to analysis was of the

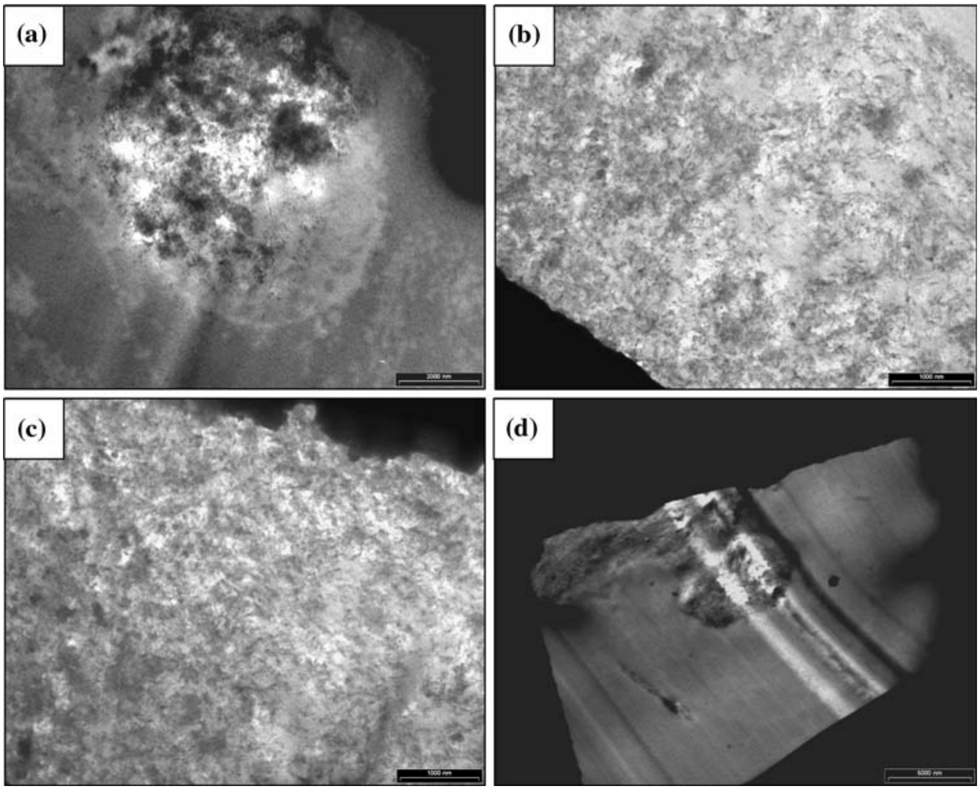

Fig. 5 TEM pictures of silicone composites loaded with **a** purified MWNTs, **b** and **c** MWNTs functionalized with 7-octenyltrichlorosilane, and **d** MWNTs functionalized with *n*-octyltrichlorosilane

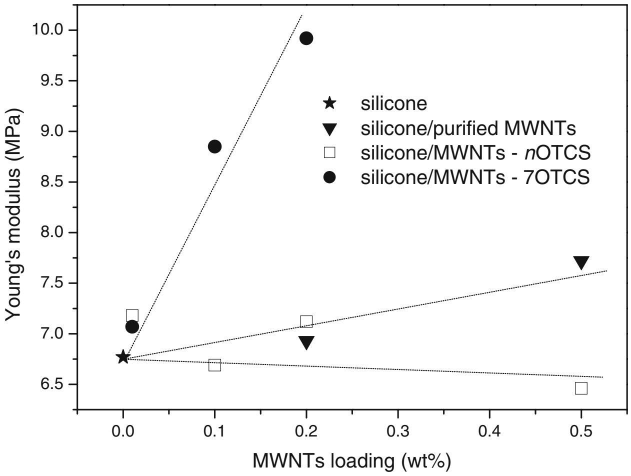

Fig. 6 Young's modulus of silicone/MWNTs composites versus the loading as determined by the various MWNTs types

order of 3 mm. The Young's modulus values result from the averaging of 10 measurements (with a 5% maximum error) made at different positions of the surface of each type of composite. Figure 6 shows the variation versus the wt% of CNTs of the Young's modulus for the different composites. Pristine silicone has a Young's modulus of 6.7 MPa (★ in Fig. 6).

The modulus of a silicon composite based on purified MWNTs increases slightly with the load, up to 7.7 MPa for 0.5 wt% of the purified MWNTs (▼). Such a low enhancement in the Young's modulus is not surprising considering the relatively poor dispersion noted in TEM images (Fig. 5a). Furthermore, the interfacial bonds that could have been established between the chemical functionalities (–COOH, >CO, –OH, …) residing at the surface of the purified MWNTs and the silicone rubber are probably too low in number and of too low effectiveness to impart a high Young's modulus to the composite.

As anticipated, in the case of *n*OTCS-loaded composites (☐), for which no dispersion has been noted, the mechanical properties of the composites are very bad, i.e., worse than the pristine silicone rubber itself, and degrade with the charge in CNTs. This has to be correlated with the presence of big aggregates which are known to have an adverse effect on the mechanical properties of composites in general [22, 23].

The situation is quite the opposite for the composite formed with nanotubes functionalized with 7OTCS (●). For instance, the Young's modulus is seen to increase from 6.7 MPa for the pristine silicone to 9.9 MPa when the silicone is loaded with only 0.2 wt% in f-MWNTs. This corresponds to a quite significant 50% enhancement of the Young's modulus for a somewhat modest charge in CNTs. Ma et al. have recently reported similar improvements on the thermomechanical properties of an epoxy/CNT composite with CNTs functionalized with 3-glycidoxypropyltrimethoxysilane [24]. As in our case, they attribute the noted improvements to the higher degree of cross-linking reactions by the epoxy end-groups on the silane–CNTs than the untreated counterparts.

Conclusion

Functionalization of MWNTs (f-MWNTS) by silanes, in particular, by chlorosilanes in this study, has been shown to have a marked benefit on their dispersion in PDMS liquids such as the components used to prepare Sylgard®184 silicone rubber. This is interpreted as due to the good compatibility between the PDMS chains present in the Sylgard®184 components and the siloxane network created at the surface of the MWNTs during their functionalization.

To prepare Sylgard®184/MWNT nanocomposites through solution processing with well-dispersed and covalently integrated CNTs in the host matrix, the siloxane network must comprise reactive functions capable of participating in the cross-linking process. Compatibility with the liquid components alone is not only insufficient but has been shown to lead to composites of drastically less quality than those obtained with the so-called purified MWNTs. Both objectives, dispersion and covalent integration of MWNTs in the silicone elastomer, have been achieved by functionalization of the MWNTs with 7-octenyltrichlorosilane. Thereby, a quite promising Young's modulus enhancement has been obtained.

As mentioned in several studies, the siloxane network created at the surface of the MWNTs through silanization favors their dispersion in polymer matrices [11, 18, 19, 24, 25]. It also offers a convenient platform to provide functions to incorporate covalently bonded f-MWNTs in the host matrix. However, such networks have been reported to be 2–3 nm thick. Most of the times, they come out thicker if no care is taken to prevent overcondensation, a situation well known in the modification of SiO_2 and metal oxide surfaces with silane-coupling agents. Considering the rich variety of existing silane molecules, it is desirable and possible to modulate further the surface properties of the MWNTs to prepare composites with higher performances (mechanical, thermal, electrical, etc.). Capitalizing on the specific reactivity of chlorosilanes, we are presently working with suitably selected monochlorosilanes with the aim of controlling the extent (thickness, coverage, etc.) of the siloxane network formed between the neighboring molecules, yet keeping the compatibility high with the surrounding medium. Special attention shall be paid to assess the relative amount of sidewall defects induced by the functionalization.

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