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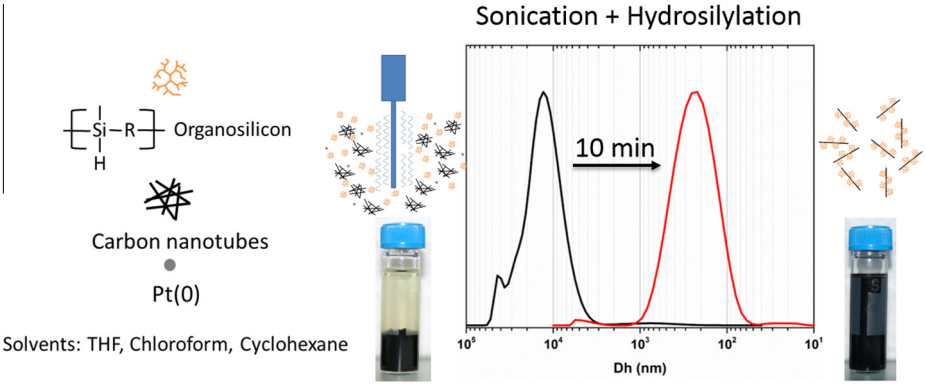
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Rapid carbon nanotubes suspension in organic solvents using organosilicon polymers

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GRAPHICAL ABSTRACT



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ABSTRACT

A strategy for a simple dispersion of commercial multi-walled carbon nanotubes (MWCNTs) using two organosilicones, polycarbosilane SMP10 and polysilazane Ceraset PSZ20, in organic solvents such as cyclohexane, tetrahydrofuran (THF), m-xylene and chloroform is presented. In just a few minutes the combined action of sonication and the presence of Pt(0) catalyst is sufficient to obtain a homogeneous suspension, thanks to the rapid hydrosilylation reaction between Si—H groups of the polymer and the CNT sidewall. The as-produced suspensions have a particle size distribution <1 μm and remain unchanged after several months. A maximum of 0.47 and 0.50 mg/ml was achieved, respectively, for Ceraset in THF and SMP10 in chloroform. Possible applications as polymeric and ceramic thin films or aerogels are presented.

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1. Introduction

Accomplishment of a homogeneous filler dispersion is the key to produce a high performing composite. The mechanical strength is improved and percolation is achieved at lower volumes. This is true in general but it assumes more significance in the case of carbon nanotubes (CNTs). With exceptional properties such as

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Young's modulus in the order of 1 TPa, electrical conductivity between 10^2 and 10^6 S/cm combined with a high aspect ratio, makes CNTs attractive for a broad range of applications. Their agglomeration-free dispersion in the matrix is important for achieving the maximum effect. Well dispersed systems can reach percolation already at 0.025 wt.% as reported by Sandler et al. for a CNT-epoxy composite [1]. On the contrary agglomerates of CNTs act as defects causing stress concentration and premature failure of the structure under mechanical load.

A common strategy for producing polymer composites is solution blending. Briefly, the polymer is added while stirring in a CNTs suspension followed by solvent evaporation. Functionalized CNTs or surfactants are used to improve the dispersion. Also in-situ-polymerization is based on the same strategy but in this case there is formation of chemical bonds between the monomer and functionalized CNT surface as reported for epoxy nanocomposites [2]. To preserve the electronic structure of the CNTs noncovalent dispersing methods were investigated to avoid the functionalization step that is reported to damage it. Another reason is the simplification of the whole process. Functionalization of CNTs involves the use of acids plus a washing/drying procedure before their effective use [3]. As reported by Bilalis et al. [4] polymers can directly dissolve untreated CNTs in solvents via noncovalent π-π and CH-π interactions [5,6] but also wrapping [7]. The polymer is adsorbed on the surface of the CNTs, avoiding the re-aggregation process in liquid media due to the steric repulsion exerted. The use of conventional un-modified polymers and to directly disperse CNTs in organic solvents via CH-π interactions seems the most interesting approach because no particular procedures have to be adopted. However, the dispersibility reported [6] is very low (below 0.020 mg/ml) for practical use in a composite. A method to improve it up to 1.235 mg/ml was found by Xu et al. in 2009 [8] using a hyperbranched polyethylene. The branched structure was suggested to cause a higher CH-π interaction enhancing the solubility. Interesting properties due to the polymer architecture were also found with dendrimers [9].

Despite all these different approaches and possibilities there are still few works about the use of organosilanes for CNTs suspension and among them almost only polydimethylsiloxane (PDMS) is investigated. To the best of our knowledge there are no reports about the use of other organosilanes as dispersants for CNTs. Among them preceramic polymers polysilazane, polyborosilane and polycarbosilane are an important class because technical ceramics such as SiC, SiCN, and SiCBN can be obtained after pyrolysis. These are also promising materials for diverse applications such as micro-electro-mechanical-system (MEMS) fabrication [10,11], anode batteries [12], harsh environment sensors [13] and high temperature resistant fibers [14]. The first study about polysilazane-CNT composites [15] was in 2004 and up to now only few others followed [16–21]. The filler dispersion in the polymer matrix is usually poorly described and realized following different methods such as functionalized CNTs, surfactants or direct sonication of the filler in organic solvents. All these techniques involve either a long procedure or are not efficient.

In this paper we report a simple one-step method for the dispersion of pre-sonicated CNTs in organic solvents. We show for the first time that preceramic polymers and in particular polycarbosilane SMP10 can be used to disperse MWCNTs thanks to the addition of Pt(0) as catalyst during sonication. The main advantage compared to other methods is the simplicity of the process. All the used products are commercially available and no additional steps such as washing, drying and functionalization are needed except solvent removal to obtain a CNT/polymer mixture ready for casting. The polymer used is in fact also the matrix of the composite and Pt(0) the catalyst to aid curing. In this way we produced a polymer-MWCNT stable suspension that can be used in various applications. The concept was then also shown to be valid for the polysilazane Ceraset.

2. Experimental procedure

2.1. Materials used

Two different types of commercially available MWCNT were used as received. Baytubes C150P (Bayer Material-Science AG, Leverkusen, Germany) possess purity >95 wt.% and tube length >1 μm. Nanocyl™ NC7000 (Nanocyl S.A., Sambreville, Belgium) possess purity >90 wt.% and average tube length of 1.5 μm. Both are produced via catalytic chemical vapor deposition (CVD) methods. More information can be found in the respective datasheets.

The two commercially available preceramic polymers (PDC polymers) used were allylhydridopolycarbosilane SMP10 (batch J20867, viscosity 51 cps Starfire Systems Inc., USA) with nominal formula $[SiH(CH_2CH{=}CH_2)CH_2]_{0.1}[SiH_2CH_2]_{0.9}$ and polysilazane Ceraset PSZ20 (Kion Corp. Pennsylvania, USA) with nominal formula $[SiCH_3(CH_2CH{=}CH_2)NH]_{0.2}[SiCH_4NH]_{0.8}$.

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution 2% in xylene (Sigma Aldrich, Switzerland), was further diluted in m-xylene to obtain a concentration of 0.1 wt.% and used as catalyst.

All the solvents used (cyclohexane, m-xylene, THF, chloroform) had a purity of >99.5% and were purchased in Switzerland from Sigma Aldrich or Carl Roth.

2.2. MWCNT de-bundling

The MWCNTs were first separated into individual nanotubes de-bundling the as purchased powder via sonication in the selected organic solvent for 2 h using a Sonoplus 2200 (Bandelin, Germany) set with cycle 9, power 20% and equipped with a titanium probe. The process was performed in a water bath cooled with ice to avoid excessive evaporation of the solvent. The solvent weight loss was compensated by adding fresh solvent to obtain a final CNT concentration of 3.9 mg/ml. Typically, a batch of about 10.5 ml of de-bundled CNT in solvent was produced each time.

2.3. Suspension preparation

The preceramic polymer was first dissolved in the organic solvent and de-bundled MWCNT added, reaching the desired CNT concentration. Finally Pt(0) catalyst was added. The mixture was first homogenized by hand and then sonicated with a VC70C ultrasonic processor (Sonics, USA) set at pulse 6 and amplitude 40% and equipped with a Vibracell VC18 probe (Sonics, USA). The suspension was stored in a refrigerator for at least 12 h to allow formation of aggregates and then centrifuged with a Universal 320 (Hettich, DE) for 30 min at 4000 rpm (2701 RCF_{MAX}). The extracted supernatant was then analyzed.

In a typical preparation, a 0.50 mg/ml CNT suspension in cyclohexane was obtained sonicating 150 μl of SMP10 added together with 3290 μl of pure cyclohexane, 514 μl of de-bundled CNT in cyclohexane and 50 μl of Pt(0) 0.1 wt.% in m-xylene. A scheme of the whole suspension preparation is presented in Fig. 1.

2.4. Characterization methods

- Fourier transform infrared spectroscopy (FT-IR) spectra were collected on a Tensor 27 (Bruker, MA, USA) pouring some sample drops on a Golden Gate ATR.

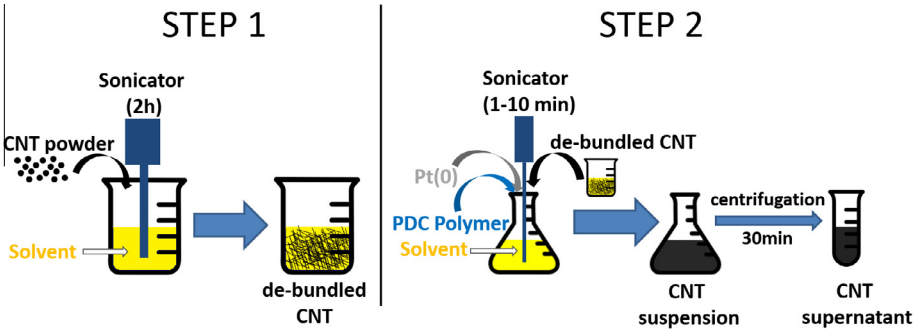


Fig. 1. Scheme of the suspension process: de-bundling of CNT powder – STEP 1 and suspension realization – STEP 2. At the end of step 2 the suspension is centrifuged and the supernatant is extracted.

- Intensity weighted particle size distribution was analyzed with a Zetasizer Nano S (Malvern, UK) by dynamic light scattering (DLS) in NIBS (non invasive back scattering) configuration and in accordance with ISO 22412 as previously described [22]. For this measurement the suspension was diluted to obtain a semi-transparent liquid. The distribution data are an average of a minimum of three different runs each one composed by 13 autocorrelation functions (ACFs) combined to a mean ACF and evaluated by the Zetasizer Software version 7.03 appendant to the Zetasizer Nano S.
- Particle size distribution of the de-bundled CNT was measured with light scattering LS320 (Beckman Coulter, USA).
- UV–vis analysis was performed in a quartz glass cuvette with a Uv-3600 (Shimadzu, Japan) operating between 200 and 850 nm. Absorbance was maintained between 0.1 and 2 in the whole range used for the calculations through proper dilution as described previously [23]. Solvent and cuvette contribution were subtracted from the resulting spectrum.
- Thermal gravimetric analysis was conducted under flowing air using a TGA/sDTA 851e (Mettler Toledo, OH, USA) and applying a 5 °C/min heating rate up to 1000 °C. The suspended CNTs were analyzed after being washed from the polymer excess. This procedure can be described as follows: the supernatant was centrifuged at 15,000 rpm (21,382 RCF_{MAX}) for at least 30–60 min until complete CNT settling. The solvent was then replaced with fresh one and the settled CNT re-dispersed for 1 min with a Vibracell VC 18 (Sonics, USA) sonication finger. This procedure was repeated three times. At the end no significative intensity differences indicating the presence of residual SMP10 between fresh and centrifuged solvent were detected with FT-IR/ATR.

^{1}H NMR spectra were recorded at 400.18 MHz on a Bruker Avance III 400 NMR spectrometer. The 1D ^{1}H NMR spectra were performed at 298 K using a 5 mm BBO Prodigy™ CryoProbe with z-gradient and 90° pulse lengths of 11.4 μs (^{1}H), 10.0 μs (^{13}C) and 13.0 μs (^{29}C). All spectra were recorded with Bruker standard pulse programs and parameter sets, and the ^{1}H chemical shifts were referenced internally using the resonance signals of cyclohexane-d_{12} at 1.38 ppm.

3. Results

3.1. MWCNT-SMP10 suspension in cyclohexane

Among the organic solvents available, cyclohexane was analyzed first for several reasons. It is a common organic solvent, both catalyst and polymer are completely soluble, and it is not miscible with water, limiting undesired hydrolysis and condensation reactions. It has a relatively low boiling point (80.7 °C) that simplifies its extraction and a high melting point (6.5 °C) that allows it to be easily stored avoiding evaporation. In addition it has low toxicity and it is cheap.

On the other hand, as is visible in Fig. 2D, CNTs have negligible solubility in it and settle in <1 h after sonication is stopped. A prolonged sonication is also ineffective to stabilize them. Similarly, when SMP10 is added to the solvent in Fig. 2E, CNT settling occurs as well. The result completely changes in Fig. 2F when Pt(0) is added to cyclohexane together with SMP10 and a dark suspension is obtained after a short sonication time. As shown in Fig. 2F the suspension is still dark after one month and has been observed to remain unchanged, without visible phase separation, for several months until the complete evaporation of the solvent. Complete CNT settling could be archived only after centrifuging it at 15,000 rpm (21,382 RCF_{MAX}) for at least 30 min.

The difference in particle size distribution of the CNT before and after the suspension step is shown in Fig. 3. Initially the distribution in the de-bundled CNT is broad, with d_{10} = 2.7 μm and d_{90} = 26.6 μm. The aggregates due to Van der Waals' interactions have a mean size of about 14.5 μm in terms of hydrodynamic diameter D_h. After the addition of SMP10, Pt(0) and sonication for a few minutes the whole distribution, measured with Dynamic Light Scattering, is shifted below 1 μm and the mean size is about 250 nm. The distribution is comparable with the one obtained by Krause et al. [22] for Baytubes dispersed with sodium dodecyl benzene sulfonate (SDDBS) and it was associated solely with the presence of single-CNTs in the solution.

3.2. Analysis of the suspension parameters

Dispersion of CNTs can be characterized using UV–vis absorption spectroscopy. Absorption values at 600 nm were recorded and directly related to the amount of single CNTs in solution according to the Lambert-Beer law $A = \log I_0/I = \varepsilon \cdot C \cdot l$ where A is the measured absorbance and C the unknown concentration. The light path length l is fixed by the experimental setup while the calculated extinction coefficient for MWCNT at 600 nm was ε_{600} = 0.0385 L/(mg cm). At this wavelength polymer and solvents are not active and the only contribution to the absorption is attributed to the presence of individual CNTs. Bundles are in fact reported to not be active in the UV–vis region [24]. The efficacy of the dispersion method was evaluated defining its extractability as previously applied to surfactant-CNT suspensions [25] and expressed as follows:

$$\%\ extractability = \frac{C}{C_0} \times 100$$

where C is the concentration of suspended MWNTs measured with UV–vis and C_0 the concentration of MWNTs originally in solvent.

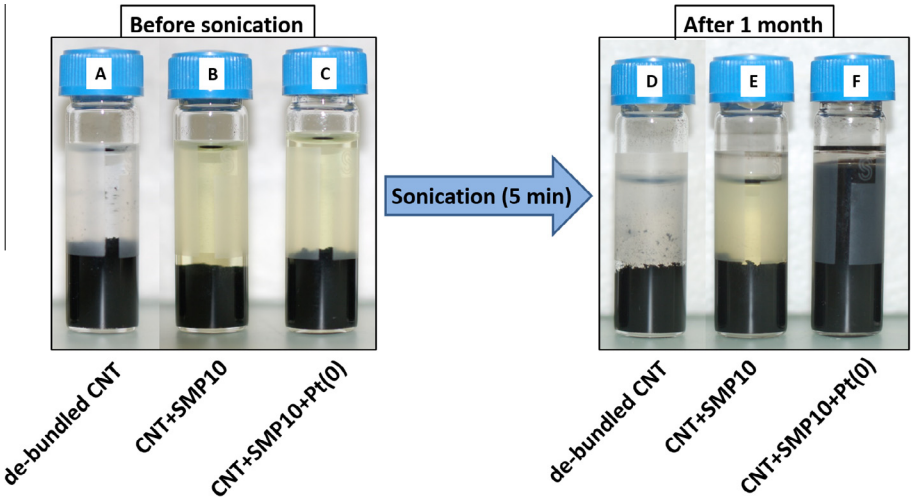


Fig. 2. CNT in cyclohexane. Effect of SMP10 and catalyst Pt(0) addition to promptly suspend MWCNT after few minutes of sonication. The difference in solvent level is due to evaporation during storage.

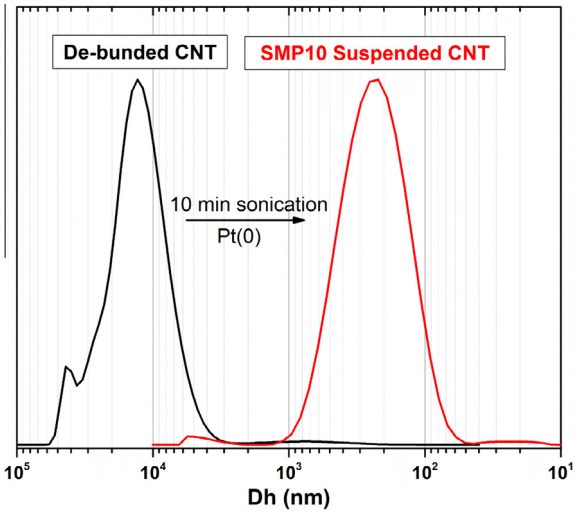


Fig. 3. Particle size distribution of CNT before and after sonication in the presence of SMP10 and Pt(0).

This parameter is used to determine the effect of the process variables and to find the optimum conditions. The extractability values were taken as an average of at least three samples each produced from a different batch of de-bundled CNTs. In Fig. 4 the influence of catalyst amount is analyzed. The solid and dashed lines compare, respectively, the extractability of the suspension produced with and without the use of Pt(0). The initial CNT concentration was 0.50 mg/ml. All the other variables such as solvent amount, polymer content, sonication time and power are kept constant. As it is visible, without catalyst the extractability of the system ranges between 1% and −7%. Aggregates are easily formed and precipitate during the centrifugation step, leaving an almost clear supernatant. On the contrary, the addition of catalyst to the system promptly improves the extractability up to 65% at 116 ppm. For higher Pt(0) amounts, up to 638 ppm, the solid curve stabilizes in a range between 60% and 65%. The considerable large standard deviation displayed is mainly attributed to the different amount and size of well separated CNT obtained during the de-bundling step that was not fully optimized in this work. As reported for surfactant based dispersions [26–28], changes in the process parameters such as probe position, power and temperature affect the degree of de-bundling. In the best case the maximum extractability on a single batch was calculated up to about 82%, that corresponds to a CNT concentration of 0.41 mg/ml. The extent of the standard deviation seems to increase also accordingly with the catalyst amount and it is explained by the higher number of reactions taking place and the increasing complexity of the system.

To determine the suspension mechanism, the effect of platinum addition was studied with TGA and it is shown in Fig. 4B. The analyzed CNTs were heated under air stream up to 900 °C with a rate of 5 °C/min. As purchased Baytubes were also analyzed for comparison. Pure carbon nanotubes decompose in air between 400 °C and 600 °C leaving a residue mass of 3% that is compatible with the >95% purity indicated in the datasheet and measured with the same method. When only SMP10 is added, MWCNTs decompose at a higher temperature between 450 °C and 600 °C with a residue mass of 36.5%. This is attributed to the presence of polycarbosilane that undergoes an oxidation process forming infusible Si—C_x—O_y as described previously [29,30]. With the addition of 290 ppm of Pt(0), red[1] line, the residues mass increases to 49% with a shift of the oxidation process at even higher temperatures between 510 and 640 °C.

The catalyst amount in the suspension was then fixed at 290 ppm to maintain a high extractability and analyze the effect of the ultrasonication time. As is visible in Fig. 5A, after 1 min the extractability is already 28% and it increases up to 65% after 10 min when the separation of CNT can be considered almost completed. Further sonication in fact improves this value to 74% but with a considerable reduced rate. To determine the optimum nominal CNT/polymer ratio and maximize the amount of suspended CNT compared to the polymer used, the initial CNT concentration was varied between 0.25 and 1 mg/ml while the SMP10 amount of 150 μl was kept constant. As visible in the blue line in Fig. 5B the optimum was calculated with a Gaussian fit to be about 1.68 wt.%, that corresponds to an initial CNT amount of 0.67 mg/ml. This gives at the end of the process a supernatant CNT concentration of about 0.33 mg/ml that corresponds to an extractability of 60%. In the same Fig. 5B the extractability displayed as a black dashed curve decreases progressively with the CNT amount from a maximum of 73% to 25%.

[1] For interpretation of color in Figs. 4 and 5, the reader is referred to the web version of this article.

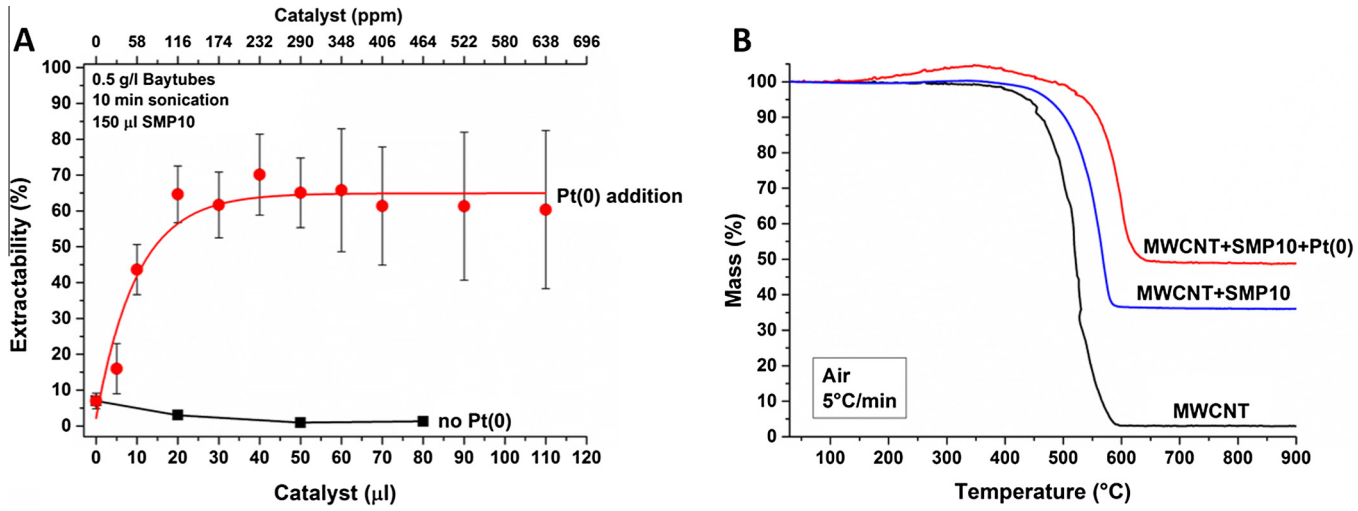


Fig. 4. (A) Effect of Pt(0) addition on the extractability of a CNT suspension in cyclohexane. (B) TGA of MWCNT + SMP10 with and without addition of 290 ppm of Pt(0) after removal of polymer excess. Pristine Baytubes mass loss is also shown.

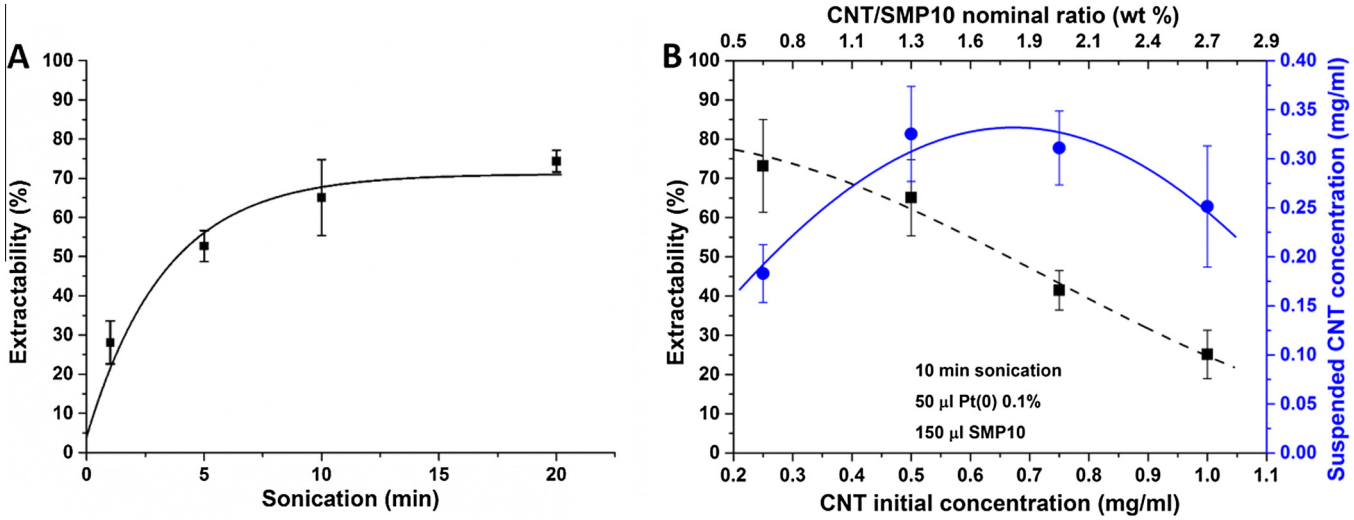


Fig. 5. Analysis of process parameters on extractability in cyclohexane. (A) Effect of sonication time and (B) effect of initial CNT concentration.

The same suspension process was also tested using commercial Nanocyl 7000 powder as MWCNT source. Starting from a concentration of 0.50 mg/ml CNT in cyclohexane in the presence of 150 µl SMP10 the effect of Pt(0) addition was tested. In the same way as Baytubes, the catalyst was fundamental to achieve a stable suspension that otherwise could not be obtained. Extractability was calculated to be 51% after 10 min sonication and mean particle size 335 nm with the whole distribution lower than 1 µm.

3.3. SMP10-MWCNT suspension in m-xylene, THF, chloroform

Starting from a CNT concentration of 0.50 mg/ml and maintaining the same process parameters (150 µl of SMP10, 290 ppm Pt(0), 10 min sonication), the effect of organic solvents other than cyclohexane on the suspension was analyzed. As shown in Fig. 6A and B sedimentation occurs in THF and m-xylene a few hours after sonication and it is independent of Pt(0) use. On the contrary in Fig. 6C a black stable solution with extractability of 90–100% and mean particle size of 350 nm could be obtained in chloroform. As shown in Fig. 6D a stable suspension is obtained in chloroform also without addition of Pt(0). In this case, despite the absence of a clear

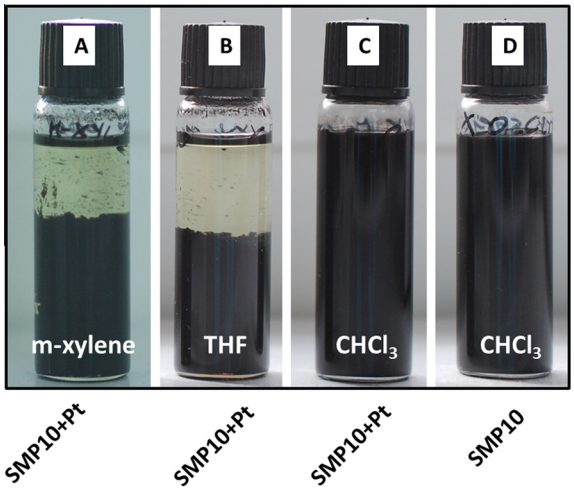


Fig. 6. SMP10-MWCNT suspensions in m-xylene, THF and chloroform 24 h after sonication. CNT initial concentration is 0.50 mg/ml.

sedimentation process aggregates together with single CNT were noticed after proper dilution.

3.4. Ceraset-MWCNT suspensions in organic solvents

In liquid form like SMP10, Ceraset PSZ20 is soluble in the same solvents and its polymer chain structure includes Si—H, C—H and vinyl groups together with N—H group characteristic of polysilazanes. The efficacy of the suspension method schematized in Fig. 1 with and without the addition of 290 ppm Pt(0) was tested in several organic solvents and the results are summarized in Table 1. Extractability and mean particle size are reported as well as the type of CNT used.

In cyclohexane and chloroform a stable CNT suspension with a particle size distribution <1 μm was obtained in the presence of Pt (0). No aggregates were formed and the extractability was 57% and 51% respectively. Without catalyst large aggregates were instead found even after centrifuging at 4000 rpm for 30 min, the suspension remained black. Similar results were obtained with Nanocyl, where mean particle size and extractability in cyclohexane were 461 nm and 49%, respectively.

In THF stable CNT suspension with mean particle size of 298 nm was obtained without addition of Pt(0). The extractability was measured to be 57% and no aggregates were noticed after dilution. With the addition of catalyst, the particle distribution remains similar with a mean size of 254 nm, but the extractability increases up to 95%.

An opposite case is represented by m-xylene, despite the use of Pt(0) complete settling and aggregation takes place soon after the sonication stops.

Table 1
Extractability and mean particle size of CNT suspensions in several organic solvents using Ceraset PSZ20.

Solvent	Catalyst 290 ppm	CNT 0.5 mg/ml	Extractability (%)	Mean size
Cyclohexane	YES	Baytubes	57	381 nm
Cyclohexane	YES	Nanocyl	49	461 nm
Cyclohexane	NO	Baytubes	–	Aggregates
Chloroform	YES	Baytubes	51	245 nm
Chloroform	NO	Baytubes	–	Aggregates
THF	YES	Baytubes	95	254 nm
THF	NO	Baytubes	57	298 nm
m-xylene	YES	Baytubes	–	Aggregates
m-xylene	NO	Baytubes	–	Aggregates

4. Discussion

4.1. MWCNT-SMP10 suspension in cyclohexane

CNT suspension using organosilicones raises several questions about the role of the catalyst and the solvents in the process. As shown in Fig. 2D a stable CNT suspension cannot be achieved in pure organic solvents such as cyclohexane even after intensive sonication. The high surface area leads the nanotubes to form agglomerates via Van der Waals forces and then precipitate over time. Common strategies to keep single nanotubes in solution are steric and electrostatic repulsion [31]. This is commonly used for nanoparticles in water, adjusting the pH to maximize the Zeta potential but cannot be used in organic solvents. The only option is to use a polymer that covers the nanoparticles avoiding their direct interaction.

From the results obtained with SMP10 we can assume that nanotube coverage is not caused by a single mechanism such as π-π interaction, covalent bonding or polymer structure but is the combination of several mechanisms working together. Starting from the point that a suspension process is a competition between the interaction of polymer-CNT and polymer-solvent, when the latter is stronger than the former, reduced or inefficient solubilization occurs [7,41]. This is the case of suspensions without Pt(0) addition. The 36.5% TGA yield in Fig. 4B obtained after the removal of excess polymer denotes that part of it adheres onto the CNT surface. This is possible if we assume the existence of a non-covalent interaction between SMP10 and CNTs. This is probably due to the abundant CH bonds in the polycarbosilane chain structure that give place to CH-π [6,8,32] interactions with the CNT sidewall. As reported by Beigbeder et al. [33] CH-π are responsible for the absorption properties of PDMS on CNT and are described as weak hydrogen bonds between soft acids and soft bases, largely due to dispersion forces and partly to charge-transfer and electrostatic forces. This interaction is probably also enhanced by the hyperbranched structure of the polycarbosilane [34] as reported for similar polymers [8,35].

SMP10 alone is insufficient to efficiently cover the nanotube surface and this causes precipitation as shown in Fig. 2E. To obtain a stable suspension a "critical surface coverage" defined as the minimum polymer amount necessary on the CNT surface to avoid CNT aggregation, must be reached. This condition is met with the addition of Pt(0) where a higher CNT coverage, displayed by a 12.5% higher yield in Fig. 4B, can be achieved. This is also visible with the stabilization of the nanotubes in Fig. 2E and the drastic change in particle size distribution in Fig. 3. The effect of Pt(0) is most likely to promote a hydrosilylation reaction by lowering the activation energy between the SMP10 Si—H groups and the CNT double bonds, thus allowing a higher and more stable coverage of the nanotubes. Pt(0) is a well-known Karstedt's catalyst specific for hydrosilylation [36], used in the curing of silicones and this reaction has already been reported to occur spontaneously at room temperature between triethylsilane and metallic SWCNT [37]. Due to the wrapping of the polymer on the nanotube, the reaction is supposed to involve only a small fraction of the Si—H groups available, those closest to the CNT wall. This would explain the absence of significative changes of the Si—H signal intensity in the ^{1}H NMR spectra (attached in the supplementary information) between the diluted polymer and the same, sonicated in the presence of 300 ppm of Pt(0) and CNT.

Starting from the TGA data the polymer amount on the nanotubes can be estimated in terms of monolayers (ML_{SiC}) using the formula reported by Shah and Raj [38].

$$ML_{SiC} = \frac{\omega_{SiC}}{1-\omega_{SiC}} \times \frac{MW_C}{MW_{SiC}} \times \left(\frac{\Omega_{SiC}}{\Omega_C}\right)^{2/3}$$

where ω_{SiC} is the ceramic yield at 900 °C without contribution of the CNT impurities, and MW and Ω are molecular weight and molar volume/Avogadro's number respectively. The subscripts denote the carbon in the nanotubes and the ceramic molecules of the TGA residues. It has to be mentioned that due to the impossibility to examine the small TGA residues and the difference that may exist between monolayer and bulk specimens pyrolysis, the above formula gives only an approximation of the polymer coverage. Due to the multitude of literature data, given by different process conditions and precursor chemistry used, we assumed for the ceramic a density between 2.4 and 2.8 g/cm^3 [39–41] and a composition ranging between $SiC_{1.19}O_{0.16}$ and $SiC_{1.16}O_{0.76}$ as reported previously for the same [42] and other precursors [43–46], within which our composition falls. The density of carbon is taken as 2.26 g/cm^3 and its atomic volume as 0.0088 nm^3. With these values ML_{SiC} is calculated to be 0.5–0.55 and 0.25–0.3, respectively with and without Pt(0) addition. This shows that there is a non-covalent interaction between polymer-nanotubes, confirming what was reported for SiCN precursor [38], and that Pt(0) addition can double the polymer

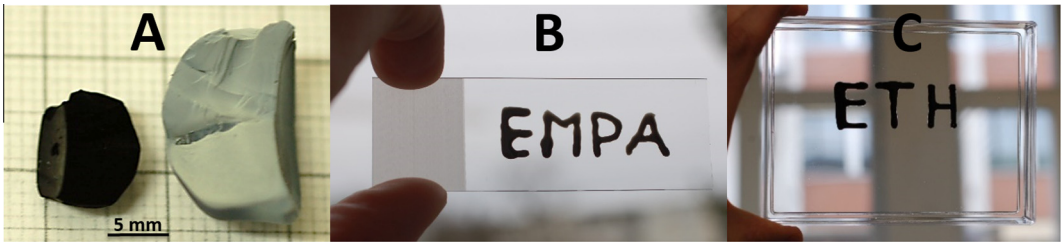


Fig. 7. Example of CNT suspension use. (A) SMP10-DVB Aerogel with 0.3% CNT filler before and after 1000 °C pyrolysis, respectively right and left. (B and C) SMP10-CNT 1 wt. % filler content used as ink respectively on glass and polystyrene substrate.

coverage on the nanotubes allowing their dispersion. The calculated values are most likely higher because the fraction of the non-covalent coverage may have been removed during the washing procedure.

The catalyst is then the key factor to stabilize the nanotubes and its amount influences the process and the extractability. In Fig. 4A after 10 min sonication the system reaches its maximum with 170–290 ppm of catalyst. This means that the CNT coverage can be completed with this optimum amount. Additional catalyst is therefore unnecessary because it will promote also side reactions in the system like polymer-polymer crosslinking.

Sonication also plays an important role in the process, because it separates agglomerates into single nanotubes and at the same time provides the necessary energy for the hydrosilylation reaction. As shown in Fig. 5 the polymer coverage process of the nanotubes proceeds rapidly and is almost complete in about 10 min. Prolonged sonication times have instead a limited effect on the extractability.

4.2. MWCNT-SMP10 suspension in THF, m-xylene and chloroform

From the results obtained in cyclohexane we can extend the concept to the other organic solvents analyzed. In THF and m-xylene the polymer-solvent interaction is stronger than for polymer-CNT and SMP10 remains dispersed in solution without or only partially adhering on the nanotubes wall. The addition of Pt(0) is uninfluential and does not help to reach the needed "critical CNT coverage" that allows CNT suspension in the specific solvent.

In the case of chloroform a dark stable suspension can be obtained without Pt(0) addition as shown in Fig. 6D. Different from the other organic solvents used, chloroform's density (1.49 g/cm^3) is almost double compared to cyclohexane (0.779 g/cm^3), THF (0.89 g/cm^3) or m-xylene (0.86 g/cm^3). Its value is also higher than the density of SMP10 (0.998 g/cm^3) and comparable with the density of MWCNT that can be ranged between 1.5 and 2.3 g/cm^3 [47]. This greatly affects the precipitation. This can be simply described by Archimedes' principle $F = g \cdot m \cdot (\rho_P - \rho_F)/\rho_P - F_D$ stating that the force exerted on an object in a liquid is proportional to the difference between its density (ρ_P) and the density of the fluid (ρ_F) minus the drag (F_D). Because partially covered ρ_P is calculated as the weighted average between polymer and CNT density resulting in an almost negligible or negative precipitation of the nanotubes.

The suspension is anyway not homogeneous, suggesting that the polymer coverage is incomplete and aggregates can be found in the supernatant. A complete coverage and uniformly dispersed single nanotubes are instead obtained after the addition of Pt(0). The high extractability values obtained are also an effect of the chloroform density that suspends a higher nanotube amount up to 0.50 mg/ml. Among these, a fraction with only partial coverage and/or still entangled is also most likely included but cannot be easily separated from the rest via centrifugation.

4.3. MWCNT-Ceraset suspensions

The use of polysilazane Ceraset confirms the results obtained with polycarbosilane SMP10. With a similar chemical structure, stable and homogeneous suspensions of MWCNT in organic solvents can be easily achieved via sonication in the presence of Pt(0). The best result was obtained in THF where nanotubes without catalyst addition could be already separated and suspended. This indicates a higher non-covalent interaction of the polymer with the CNT instead with the solvent. In this way the polymer can adhere onto the CNT wall and oppose the Van der Waals force via steric repulsion. The effectiveness in dispersing CNT via simple sonication in THF + Ceraset was already reported by Katsuda et al. [16] to produce SiCN-CNT ceramic composites but the dispersion process was not analyzed. In Table 1 it is shown that with the use of Pt(0) the fraction of well dispersed CNT increases from 57% to 95% thanks to the induced hydrosilylation reaction.

In cyclohexane and chloroform a stable suspension was obtained only with Pt(0) addition indicating that it was fundamental to reach the necessary "critical surface coverage".

Similar to SMP10, with Ceraset not only Baytubes but also Nanocyl were successfully suspended in cyclohexane. This suggests that the suspension method is generally valid and not specific for a specific type of CNT. Of course, this will lead to different extractabilities according to the CNT characteristics such as purity, dimension and chirality.

5. Conclusions

We have demonstrated a simple straightforward strategy for the suspension of MWCNT in organic solvents with the use of preceramic polymers and Pt(0) catalyst. Nanotube suspension is directly achieved in about 10 min in one-step without the necessity of previous functionalization. The mechanism and the principal findings can be summarized as follows:

(1) Pt(0) is fundamental to achieve a stable suspension in organic solvents. The use of SMP10 or Ceraset alone is not sufficient to efficiently suspend the CNT and better results were always achieved when using Pt(0).
(2) The suspension mechanism is explained as the sum of a non-covalent assembly of the polymer on the CNT surface due to CH-π interaction, plus the hydrosilylation reaction between Si—H group of the polymer and C=C of the nanotube catalyzed by Pt(0). Non-covalent interaction was in fact demonstrated to not efficiently cover the nanotubes and assure sufficient steric repulsion. On the contrary with the addition of catalyst a higher and stable polymer coverage of the nanotubes can be achieved. When this is higher than a certain "critical coverage value" defined as the minimum polymer amount necessary on the CNT surface to avoid CNT aggregation, a stable suspension is obtained.

(3) Using SMP10 the higher CNT concentrations were, respectively, 0.50 mg/ml in chloroform and 0.41 mg/ml in cyclohexane. For Ceraset 0.47 mg/ml, 0.29 mg/ml and 0.26 mg/ml were obtained, respectively, in THF, cyclohexane and chloroform. In all the analyzed suspension the particle size distribution was <1 μm.
(4) This novel method is a simple and quick alternative to surfactant and CNT functionalization in organosilicon composites production. In addition it can be easily upscaled, all the materials are relatively cheap and commercially available and more importantly it can most likely be extended to polymer and molecules with the same functional groups.

6. Outlook and possible applications

The analyzed CNT-polymer suspensions process allows to have a stable and homogeneous distribution of filler in different organic solvents such as cyclohexane, chloroform and THF that can be used for different applications. As recently reported by Sorarù et al. [48] and Zera et al. [49] highly porous aerogels are produced from preceramic polymers crosslinked with divinylbenzene (DVB) in suitable solvents. The cited method can be applied also to the CNT suspension to produce a novel MWCNT-polycarbosilane composite aerogel. The sample in Fig. 7A has a filler content of 0.3% and was realized as proof of concept. The grayish uniform color instead of the characteristic white of SMP10-DVB aerogel suggests the effective incorporation of the filler. In the same picture is also visible half of the aerogel after pyrolysis in Argon atmosphere at 1000 °C. The shrinkage due to the gas released during the process is about 30% linear but the porous structure is maintained. Polymer derived ceramics (PDCs) carbon-rich aerogels are studied as suitable material for Li-ion batteries because as described by Pradeep et al. [50] the porous nature allows for fast ionic transport and helps to accommodate the structural changes which in turn allow a stable performance during repeated lithiation/delithiation.

Further applications of the dispersion can be found after the removal of the solvent. As shown in Fig. 7 the obtained black liquid can be easily spread on different surfaces like glass and polystyrene or cast in a mould to realize a polymer-CNT composite with desired shape. The Pt(0) already included in the suspension process allows the mixture to cure at ambient temperature as described by Blum et al. [51]. The maximum achievable filler load was 1.4 wt.% and 1.3 wt.% for SMP10 in chloroform and Ceraset in THF, respectively. In comparison, 1.2 wt.% is reported to be sufficient to reach percolation in PDMS [52]. Furthermore, the preceramic polymeric matrix can be converted into a SiC-CNT or SiCN-CNT ceramic matrix composite via pyrolysis [20]. Fields of interest are ceramic fibers [53], ceramic MEMS [54] and biomedical devices [55].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.02.050.

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