Journal of Colloid and Interface Science 470 (2016) 123–131

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

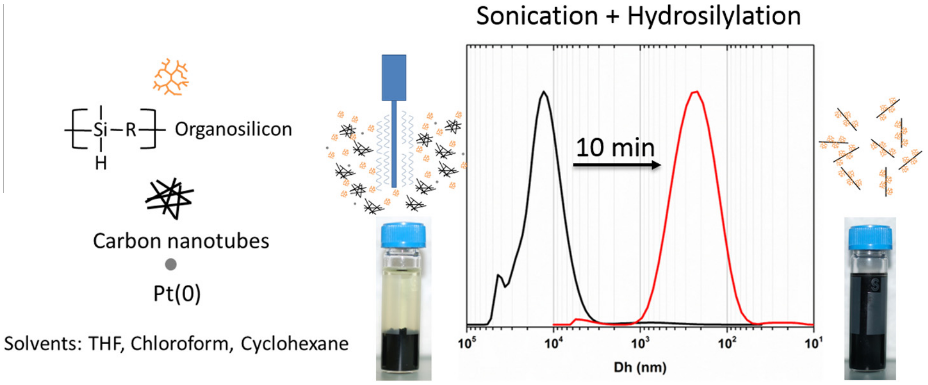
journal homepage: www.elsevier.com/locate/jcis

Rapid carbon nanotubes suspension in organic solvents using organosilicon polymers

Federico Dalcanale[a,b,*], Jonas Grossenbacher[c], Gurdial Blugan[a], Maurizio R. Gullo[c], Jürgen Brugger[c], Hendrik Tevaearai[d], Thomas Graule[a], Jakob Kuebler[a]

[a] *Empa, Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Duebendorf, Switzerland*
[b] *Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland*
[c] *Microsystems Laboratory, EPFL, Station 17, CH-1015 Lausanne, Switzerland*
[d] *Clinic for Cardiovascular Surgery, Inselspital Berne, Berne University Hospital and University of Berne, Berne, Switzerland*

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 January 2016
Accepted 22 February 2016
Available online 23 February 2016

Keywords:
MWCNT suspension
Hydrosilylation
Polycarbosilane
Polysilazane
Aerogel

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.

© 2016 Elsevier Inc. All rights reserved.

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

---

* Corresponding author at: Empa, Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, Duebendorf, Switzerland.

E-mail addresses: dalca82@hotmail.com (F. Dalcanale), jonas.grossenbacher@epfl.ch (J. Grossenbacher), Gurdial.Blugan@empa.ch (G. Blugan), rosario.gullo@rudevoltage.ch (M.R. Gullo), juergen.brugger@epfl.ch (J. Brugger), Hendrik.TevaearaiStahel@insel.ch (H. Tevaearai), Thomas.Graule@empa.ch (T. Graule), Jakob.Kuebler@empa.ch (J. Kuebler).

http://dx.doi.org/10.1016/j.jcis.2016.02.050
0021-9797/© 2016 Elsevier Inc. All rights reserved.

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 SiBCN 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.

Download English Version:

https://daneshyari.com/en/article/606306

Download Persian Version:

https://daneshyari.com/article/606306

Daneshyari.com