



## The effects of highly structured low density carbon nanotube networks on the thermal degradation behaviour of polysiloxanes



James P. Lewicki\*, Marcus A. Worsley, Rebecca L.F. Albo, Jasmine A. Finnie, Michael Ashmore, Harris E. Mason, Theodore F. Baumann, Robert S. Maxwell

Lawrence Livermore National Laboratory, Chemical Sciences Division, 7000 East Avenue, Livermore, CA 94510, USA

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### ABSTRACT

Carbon nanotube-carbon aerogel (CNT-CA) networks are a member of a novel class of ultra-low density, high surface area, hierarchically structured, carbon-based materials possessing unique mechanical and physical properties. Through the secondary incorporation of a polymer matrix into these aerogel systems it is now possible to form intercalated polymeric hybrid CNT-CA composite materials with polymer to carbon surface internal surface contact areas in the order of  $\sim 600 \text{ m}^2 \text{ g}^{-1}$  at carbon loadings as low as  $\sim 1.5 \text{ wt } \%$ . Reported here is the synthesis of a series of well-defined poly(dimethylsiloxane) (PDMS)/CNT-CA composite systems, their characterization and the in-depth analysis of the effects of the carbon architecture on the thermal stability and degradation behaviour of the of the PDMS matrix. The results of degradative thermal analysis using both pyrolysis gas-chromatography/mass spectrometry (py-GC/MS) and thermogravimetric analysis (TGA), clearly demonstrate that the presence of the CNT-CA scaffold within the PDMS matrix greatly increases the thermal stability of the system and drives the matrix towards calcination at temperatures above  $600 \text{ }^\circ\text{C}$ . Subsequent characterization of the residual materials using a combination of fast magic angle spinning solid-state nuclear magnetic resonance (Fast-MAS NMR), energy dispersive X-ray spectroscopy (EDAX) and electron microscopy have demonstrated that the improvements in thermal stability are concurrent with the relative loading of carbon nanotubes within the aerogel matrix, that the PDMS matrix is being driven towards the formation of increased levels of  $\text{SiO}_2$  on degradation and that the preferential calcination effect is a function of the unique high surface area fibular network structure of the CNT-CA monoliths.

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### 1. Introduction

Carbon nanotubes possess a number of intrinsic properties that make them potentially, highly desirable as filler materials and physical property modifiers in the design of the next generation of polymeric composites and hybrid materials. CNTs can have electrical conductivities as high as  $1 \times 10^6 \text{ S m}^{-1}$  [1], thermal conductivities as high as  $3000 \text{ W m}^{-1} \text{ K}^{-1}$  [2], elastic moduli of the order of  $1 \text{ TPa}$  [3], and are extremely flexible [4]. Unfortunately, the realization of these properties in macroscopic forms, such as in practical advanced polymer/CNT composites, has been limited due to the inherent problems associated with the effective, uniform dispersion of CNTs as a heterogeneous 2nd phase within a polymer matrix

[5–7]. An alternative to the dispersion approach for the design of new composite systems that was originally suggested by Chen et al. in 2006 [8] and was more recently demonstrated by the authors [9], is the use of a low-density, CNT/aerogel foam as a scaffold that can be intercalated by the polymer matrix.

We have extensive expertise in the synthesis and development of such ultralow-density CNT-based aerogel foams (CNT-CAs) and have reported the exceptional electrical and mechanical properties of this unique class of materials [10,11]. In these nano-foams systems, carbon nanoparticles are used as a binder to crosslink randomly oriented bundles of single-walled CNTs. These CNT-CAs have been shown to simultaneously exhibit increased stiffness and high electrical conductivity even at densities approaching  $1 \times 10^{-2} \text{ g cm}^{-3}$  [10]. The CNT-CA materials synthesized have also been shown to be highly thermally stable, maintaining their structural architecture and integrity (under non-oxidative conditions) up to temperatures approaching  $1600 \text{ }^\circ\text{C}$  and have been shown to be unaltered by exposure to extremely low temperatures

\* Corresponding author. Tel.: +1 925 423 1115; fax: +1 44 141 548 4822.

E-mail addresses: [lewicki1@llnl.gov](mailto:lewicki1@llnl.gov), [jamespawellewicki@googlemail.com](mailto:jamespawellewicki@googlemail.com) (J. P. Lewicki).

during immersion in cryogenic liquids [12]. More recently the authors have also reported the synthesis of the first CNT-CA polymer composites using a commercial platinum-cured two part silicone resin (Dow Corning Sylgard 184) as the polymer matrix. The resultant composite system was shown to exhibit electrical conductivities over  $1 \text{ S cm}^{-1}$  and a 300% increase in the elastic modulus with as little as 1 vol% nanotube content [9].

Despite this progress in the synthesis of CNT-CA-polymer composite materials, the characterization of their chemical and physical properties has been somewhat hampered by the limitations of the commercial elastomer formulations used as the polymer matrix and have focused only on the measurement of the composite systems electrical conductivities/bulk mechanical properties [9]. To date, there have been no published data on the thermal stability and degradation behaviour of these systems – as the complex, highly filled and poorly described structure of the commercial silicone formations utilized [13] have complicated the interpretation of any thermal/chemical stability measurements or investigations of motional dynamics and relaxation behaviour.

However, through the use of a simple, structurally well-defined model polymer matrix, many of these complications which limit the mechanistic investigation of these important and novel systems may be removed.

It is well established that poly(siloxanes) thermally degrade above their ceiling temperature (c.f. linear PDMS:  $110^\circ\text{C}$ ) primarily via terminal and internal chain backbiting reactions [14–17] to yield a distribution of cyclic monomers, where the hexamethylcyclotrisiloxane or 'D<sub>3</sub>' cyclic monomer is the thermodynamic and therefore most abundant product. It is well known that the thermal stability of polysiloxanes is sensitive to the presence of Lewis acids/bases [17,18] and organo-metallic catalysts [19]. Additionally, the overall degradation pathways of polysiloxanes have been shown to be remarkably resistant to change due to additives, filler materials, catalyst residues or other contaminants [20]. Broadly speaking, a polysiloxane will always thermally degrade above its ceiling temperature to yield 30–80% of the D<sub>3</sub> cyclic and tailing distribution of higher cyclics from D<sub>4</sub> to D<sub>20–30</sub>. This overall mechanism is well established and well understood [17,21,22]. Significantly less is known, however, about the effects of more exotic additives, fillers and heterogeneous secondary phases on the physical and chemical mechanisms of silicone degradation. Indeed, the authors have shown that poly(dimethylsiloxane) (PDMS) elastomers which physically incorporate nano-scale fillers, while still forming the D<sub>3</sub> cyclic as the major product of degradation, have a significantly altered profile of *minor* degradation products [23]. Additionally we have recently shown that aspects of a silicone network structures (network modality, number of free chain ends, cross-link density etc.) can quantifiably alter the statistical distributions of higher cyclic degradation products [24].

In this work we report the synthesis of a series of PDMS/CNT-CA composites through the use of a well-defined model end-linked PDMS network elastomer as the polymer matrix for CNT-CA nanofoams. The thermal stability and mechanistic thermal degradation behaviour of a series of PDMS/CNT-CA composites have been studied through the use of TGA, py-GC/MS, solid-state NMR, EDAX and SEM. By using a simple PDMS network of known structure, we can report for the first time and without obfuscation, an in-depth study of the thermal degradation behaviour of these unique composite materials.

## 2. Experimental

### 2.1. Materials

All reagents were used without further purification. Resorcinol (99%) and formaldehyde (37% in water) were purchased from

Aldrich Chemical Co. Sodium carbonate (anhydrous) was purchased from J.T. Baker Chemical Co. Highly purified CNTs were purchased from Carbon Solutions, Inc. Vinyl terminated PDMS of average molar mass  $28 \text{ Kg mol}^{-1}$ , Poly(methylhydrosilane) of average molar mass  $2.45 \text{ Kg mol}^{-1}$ , tetravinyl-tetramethylcyclo-tetrasiloxane and a platinum-cyclovinylnmethylsiloxane complex were all purchased from Gelest Inc.

### 2.2. Preparation of CNT-CA nanofoams

Nanofoams were prepared using traditional organic sol-gel chemistry [25]. In a typical reaction, purified CNTs (Carbon Solutions, Inc.) were suspended in deionized water and thoroughly dispersed using a VWR Scientific Model 75T Aquasonic sonication bath (sonic power  $\sim 90 \text{ W}$ , frequency  $\sim 40 \text{ kHz}$ ). The concentration of CNTs in the reaction mixture ranged from 0 wt% to 1.3 wt%. To determine the optimal conditions for CNT dispersion, a range of sonication times (4–24 h) were evaluated. Once the CNTs were dispersed, resorcinol (1.235 g, 5.6 mmol), formaldehyde (1.791 g, 11.1 mmol), and sodium carbonate catalyst (5.95 mg, 0.028 mmol) were added to the reaction solution. The resorcinol to catalyst ratio (R/C) employed for the synthesis of the composites was 200. The sol-gel mixture was then transferred to glass moulds, sealed and cured in an oven at  $85^\circ\text{C}$  for 72 h. The resulting gels were then removed from the moulds and washed with acetone for 72 h to remove water from the pores of the gel network. The wet gels were subsequently dried with supercritical CO<sub>2</sub> and pyrolysed at  $1050^\circ\text{C}$  under a N<sub>2</sub> atmosphere for 3 h. The composite materials were isolated as black cylindrical monoliths. Foams with CNT loadings ranging from 0 to  $\sim 80 \text{ wt\%}$  were prepared by this method. For comparison purposes, pristine carbon aerogels without CNTs were also prepared using the method described above without the addition of CNTs.

### 2.3. Preparation of PDMS/CNT-CA composites

For the purpose of this study, an end-linked, hybrid tetra/comb crosslinked 'model' network was developed that formed via a platinum mediated vinyl addition reaction between vinyl terminated poly(dimethylsiloxane) (PDMS), 2 Wt. % tetravinyl-tetramethylcyclo-tetrasiloxane (which acts as a cure rate moderator) and a stoichiometric level of an oligomeric poly(methylhydrosilane). This network formulation was designed to have an initially low starting viscosity, a pot-life of  $\sim 4$  days at room temperature and a high final crosslink density. These properties make it an ideal material for controlled intercalation into the CNT-CA monoliths.

In order to prepare a PDMS/CNT-CA composite system, 9.8 g of vinyl terminated PDMS and 0.2 g of tetravinyl-tetramethylcyclo-tetrasiloxane were combined with a stoichiometric level of poly(methylhydrosilane) crosslinker in the presence of 10 ppm of a Pt cyclovinylnmethylsiloxane complex and mixed for 30 s using a Flactek™ Speedmixer off-axis centrifugal mixer at a rate of 2500 rpm. The mixed resin was then cooled in an ice-bath to a temperature of  $5^\circ\text{C}$ . A CNT-CA monolith was immersed fully into the cooled resin and placed under vacuum for 2 h at  $5^\circ\text{C}$  to begin the process of exchanging the air in the monolith with the resin mixture. When bubbling was observed to cease from the monolith in the resin bath, the sample was brought up to atmospheric pressure, agitated gently and returned to vacuum. Five such cycles were repeated to ensure that the polymer resin had fully penetrated the nanofoam matrix. Once the intercalation stage was completed, the resin containing the CNT-CA monolith was brought up to a temperature of  $50^\circ\text{C}$  and allowed to cure for 24 h to form a solid elastomeric block. The cured, intercalated monolith was

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