Carbon nanotube-enhanced carbon-phenenolic ablator material.

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Reentry heat shields: Overview

### Reusable

- **Space Shuttle**
  - Reinforced C-C wing leading edges and nose tip
  - Silica fiber-based porous tiles
  - Designed for low earth orbit reentry with ~7.7 km/s velocity
  - Heating rate <50 W/cm²
  - Max. temperature <1800 K
  - Fragile...

### Non-reusable ablators

- **Apollo: Avcoat 5026**, a low-density glass-filled epoxy-novolac system
  - Reentry velocity of ~10.7 km/s
  - Heating rate < 500 W/cm².
  - Max. temperature ~3000 K
  - Heavy...

- **Orion requirements:***
  - Return from Mars, Earth reentry:
  - Velocity 12-14 km/s
  - Heating rate <2000 W/cm²
  - Max T ~3000K
  - Low Weight
  - PICA has been selected for Orion lunar return

- **Stardust: PICA (phenolic impregnated carbon ablator)**
  - The highest Earth reentry velocity so far ~12.9 km/s (!)
  - Heating rate <1200 W/cm²
  - Max T ~3000 K
What is PICA

- Easily manufactured, up to 6 m diameter.
- Capable of heat rates to 2,000 W/cm².
- Opaque to shock layer radiation.
- Affords some degree of space radiation shielding.

- Char which can withstand severe aerodynamic shear and does not spall.
- Micrometeoroid and orbital debris (MMOD) impact tolerant.

Demonstrated up to ~1 m diameter
Tested up to 1600 W/cm²
Reasonably
Components are light atoms. Much better compared to silica-based materials
There’s room for improvement

There’s room for improvement
Rationale for introduction of nanotubes into PICA

Nanotubes can improve strength of phenolic resin that binds carbon fibers together.

Expected outcome:
• Improved overall strength (tolerant to higher aerodynamic shear, dynamic pressure and spallation).
• Improved micrometeoroid tolerance (if we can couple MMOD impact energy to nanotubes).

Mechanism:
• Ordering of the polymer matrix on the nanotube surface. This effect is well known in nanoclay-reinforced epoxies. Good dispersion of nanotubes is necessary to maximize interface.
• Covalent bonding or mechanical anchoring of chemically functionalized nanotubes to the polymer matrix.

MD simulation of PE molecules surrounding NT
Chenyu Wei* and Deepak Srivastava
Nano Lett., Vol. 4, No. 10, 2004
Rationale for functionalization:

• Durite SC-1008 phenolic is a partially crosslinked resole-type resin thinned with isopropyl alcohol (~30%)

• It is dissolved in ethylene glycol for impregnation into carbon fiberform

• Neat nanotubes are not compatible with polar solvents (ethylene glycol, water, etc.) since surface is sp² hybridized carbon. Neat nanotubes will exist as large bundles / aggregates, interface area will be minimal.

• We need to put polar groups on the nanotube surface to make them soluble in ethylene glycol / phenolic system. 
• It is preferable that these groups can bond or mechanically anchor to phenolic.
HiPco SWNT functionalization

1. Phenylation of nanotubes by benzoyl peroxide. Followed by sulfonation with oleum
~1:20 C atoms in nanotube have phenyl rings attached
Soluble and stable in water and polar solvents up to 0.05% concentration, aggregation observed at higher concentration.

Liang, F.; Beach, J. M.; Rai, P. K.; Guo, W.; Hauge, R. H.; Pasquali, M.; Smalley, R. E.; Billups, W. E.
Chem. Mater.; 2006; 18(6); 1520-1524

2. Nanotubes reacted with lauroyl peroxide.
Wendy Fan, Tane Boghozian, Brett A. Cruden, and Pasha Nikolaev, in press.
This is a first step. Work in underway to improve solubility and chemical compatibility of nanotubes functionalized by this process

3. Control sample: purified HiPco nanotubes
PICA manufacturing

- **stock solution**: 20% vol phenolic in ethylene glycol
- **stock solutions**:
  1. NT-Ph-SO$_3$-Na$^+$
  2. NT-LP
  3. NT-purified in ethylene glycol

Homogenized ~10 min + sonicated ~30 min,

- **Impregnated into Fiberform**
  - TEM, SEM imaging
- **Cast for optical imaging (liquid)**
  - Cured for load transfer measurements
Optical microscopy

(1) NT-Ph-SO$_3^-$Na$^+$ in EG / phenolic

(2) NT-LP in EG / phenolic

(3) Purified HiPco in EG/phenolic

(1) NT-Ph-SO$_3^-$Na$^+$ in EG / phenolic after vacuum outgassing (isopropyl alcohol removed)
SEM

Typical low magnification image of PICA

(1) NT-Ph-SO$_3$-Na$^+$ in PICA

(2) NT-LP in PICA

(3) Purified HiPco NT in PICA
(3) Purified HiPco NT in PICA
TEM

(2) NT-LP in PICA
(1) NT-Ph-SO₃⁻Na⁺ in PICA
Raman load transfer test

NT Raman G\(^+\) frequency shifts under strain. Strain in the matrix is measured independently with strain gage.

For chiral NTs (semiconducting)

\[
\frac{\Delta \omega}{\omega_0} \approx -\gamma(1 - \nu_t)e_z,
\]

- \(\gamma \approx 1.24\) - Grueneisen parameter
- \(\nu_t \approx 0.19\) - NT Poisson ratio
- \(e_z, e_{ci}\) - strain along nanotube axis and circumference

S. Reich et al., PRB 61, 13389 (2000),
Raman line shift, % vs. strain

Load transfer in NT-Ph-SO3Na+: ~80% of maximum
~6 times better than in purified HiPco

Results for NT-LP will follow.
Conclusions

- NT-Ph-SO3-Na⁺ - seems to work well
- Good dispersion
- Good load transfer

- NT-LP – dispersion not as good
- Still need the load transfer test

Future work:

**TESTING:**

- Arc-jet tests
- Char strength tests
- MMOD impact tests

- NT-LP – further work to graft polar groups

- Scale-up of all processes.