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 ~3000K
- 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.


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

Homogenized ~10 min + sonicated ~30 min,

Impregnated into Fiberform

TEM, SEM imaging

stock solutions
1. NT-Ph-SO$_3$-Na$^+$
2. NT-LP
3. NT-purified in ethylene glycol

Cast for optical imaging (liquid)

Cured for load transfer measurements
Optical microscopy

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

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

(2) NT-LP in EG / phenolic

(3) Purified HiPco in EG/phenolic
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
TEM

(1) NT-\text{Ph-SO}_3\cdot\text{Na}^+ \text{ 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)

$$\frac{\Delta \omega}{\omega_0} \approx -\gamma (1 - \nu_t) \varepsilon_z,$$

$\gamma \approx 1.24$ - Grueneisen parameter
$
\nu_t \approx 0.19$ - NT Poisson ratio
$
\varepsilon_z, \varepsilon_{ci}$ - strain along nanotube axis and circumference

S. Reich et al., PRB 61, 13389 (2000),
Load transfer in NT-Ph-SO3·Na⁺:
~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.