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
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

**Preparation Steps**
- Homogenized ~10 min + sonicated ~30 min,

**Processing Steps**
- 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 after vacuum outgassing (isopropyl alcohol removed)

(2) NT-LP in EG / phenolic

(3) Purified HiPco in EG/phenolic
Typical low magnification image of PICA

(1) NT-Ph-SO₃⁻Na⁺ in PICA

(2) NT-LP in PICA

(3) Purified HiPco NT in PICA
(3) Purified HiPco NT in PICA
(2) NT-LP in PICA
TEM

(1) NT-Ph-SO$_3$·Na$^+$ in PICA
Raman load transfer test

NT Raman G\textsuperscript{+} frequency shifts under strain. Strain in the matrix is measured independently with strain gage.

For chiral NTs (semiconducting)

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

\(\gamma = \sim 1.24\) - Grueneisen parameter
\(\nu_t = \sim 0.19\) - NT Poisson ratio
\(\epsilon_z, \epsilon_{ci}\) - 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.