Carbon nanotube-enhanced carbon-phenenolic ablator material.

P. Nikolaev[1], M. Stackpoole[3], W. Fan[4], B. A. Cruden[4], M. Waid[2], P. Moloney
S. Arepalli[1], J. Arnold[4], H. Partridge[5], L. Yowell[2]

1. ERC Inc. / NASA Johnson Space Center
2. NASA Johnson Space Center
3. Eloret Corporation / NASA Ames Research Center
4. University Affiliated Research Center, University of California, Santa Cruz / NASA Ames Research Center
5. NASA Ames Research Center

S4800 20.0kV 7.6mm x50.0k SE(U)

Reentry heat shields: Overview

Reusable

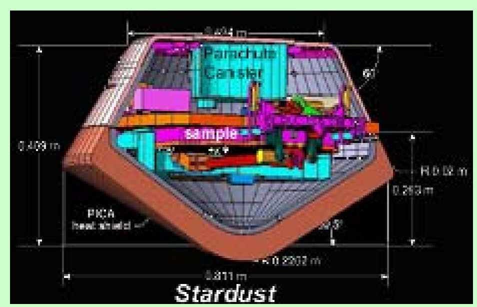
Space Shuttle
Reinforced C-C wing leading edges and nose tip
Silica fiber-based porous tiles
Designed for low earth orbit reentry with ~7.7 km/s velocity
Heating rate <50 W/cm^2
Max. temperature <1800 K
Fragile…

Orion requirements:
Return from Mars, Earth reentry:
Velocity 12-14 km/s
Heating rate <2000 W/cm^2
Max T ~3000K
Low Weight
PICA has been selected for Orion lunar return

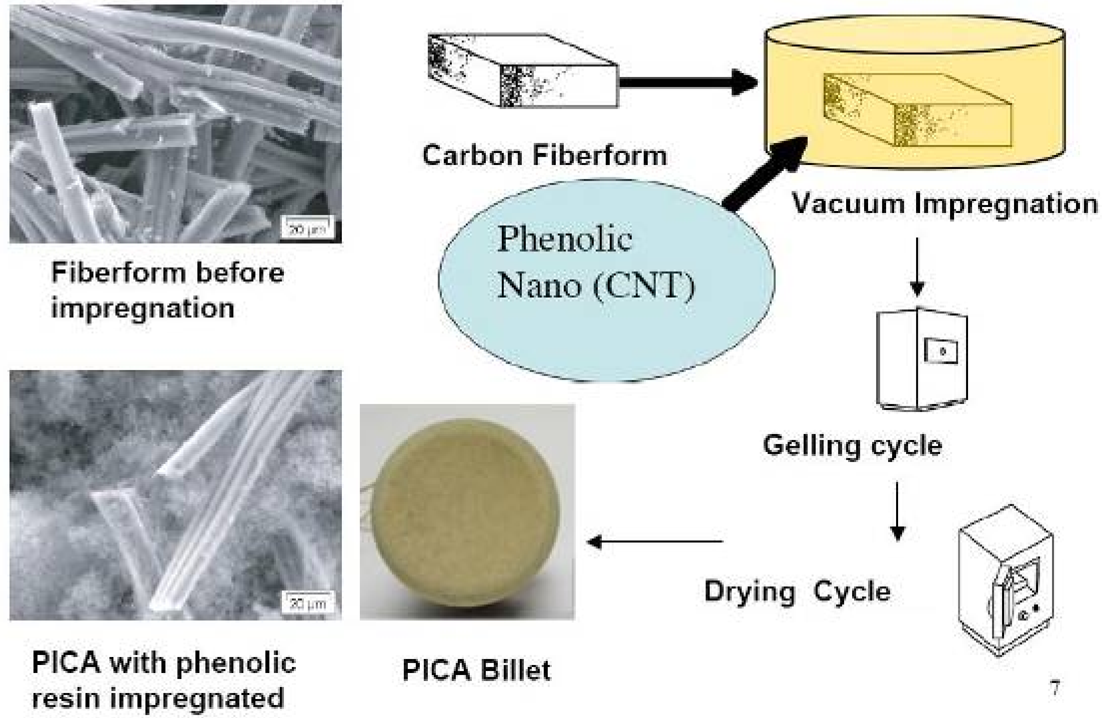
Non-reusable ablators

Apollo: Avcoat 5026, a low-density glass-filled epoxy-novolac system
Reentry velocity of ~10.7 km/s
Heating rate < 500 W/cm^2.
Max. temperature ~3000K
Heavy…

Stardust: PICA (phenolic impregnated carbon ablator)
The highest Earth reentry velocity so far ~12.9 km/s (!)
Heating rate <1200 W/cm^2
Max T ~3000 K



What is PICA



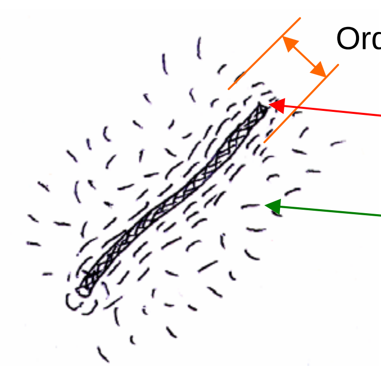
•Easily manufactured, up to 6 m diameter.	Demonstrated up to ~1 m diameter
•Capable of heat rates to 2,000 W/cm^2.	Tested up to 1600 W/cm^2
•Opaque to shock layer radiation.	Reasonably
•Affords some degree of space radiation shielding	Components are light atoms. Much better compared to silica-based materials
•Char which can withstand severe aerodynamic shear and does not spall.	There's room for improvement
•Micrometeoroid and orbital debris (MMOD) impact tolerant	There's room for improvement

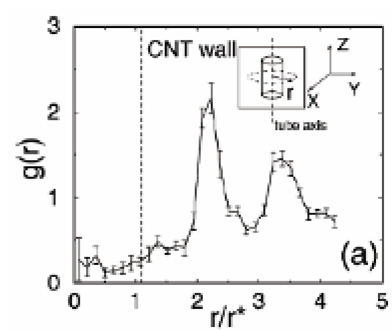
Rationale for introduction of nanotubes into PICA

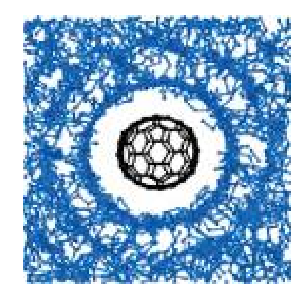
Nanotubes can improve strength of phenolic resin that binds carbon fibers together.

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%)

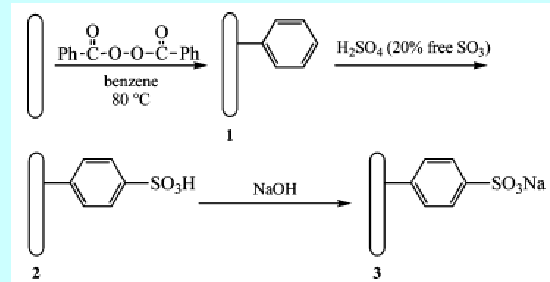
- It is dissolved in ethylene glycol for impregnation into carbon fiberform

- Neat nanotubes are not compatible with polar solvents (ethylene glycol, water, etc.) since surface is sp^2 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

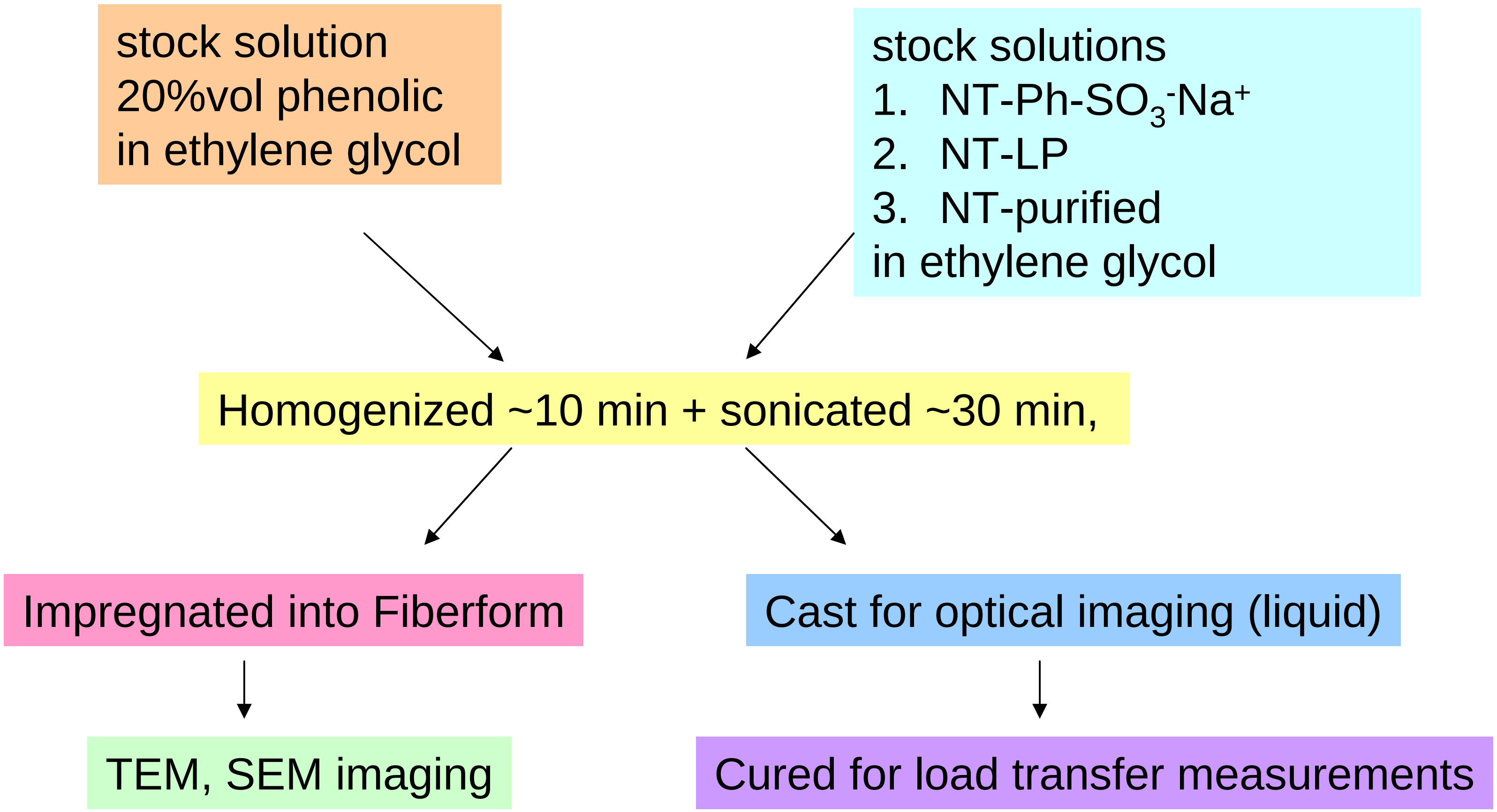
2. Nanotubes reacted with lauroyl peroxide.

Wendy Fan, Tane Boghozian, Brett A. Cruden, and Pasha Nikolaev, in press.

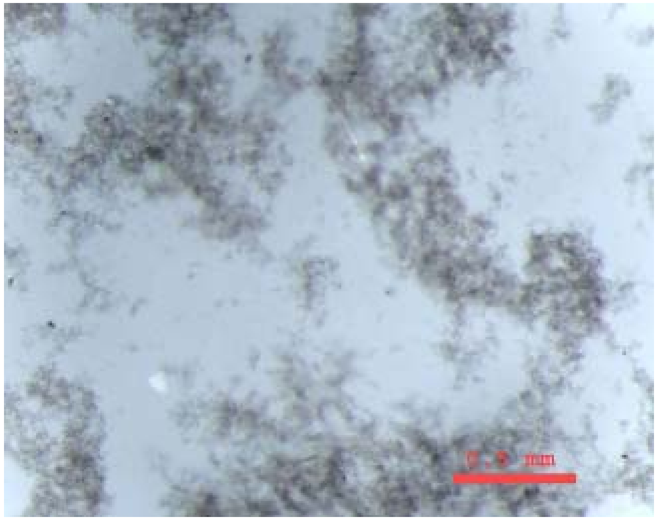
This is a first step. Work in underway to improve solubility and chemical compatibility of nanotubes functionalized by this process

3. Control sample: purified HiPco nanotubes

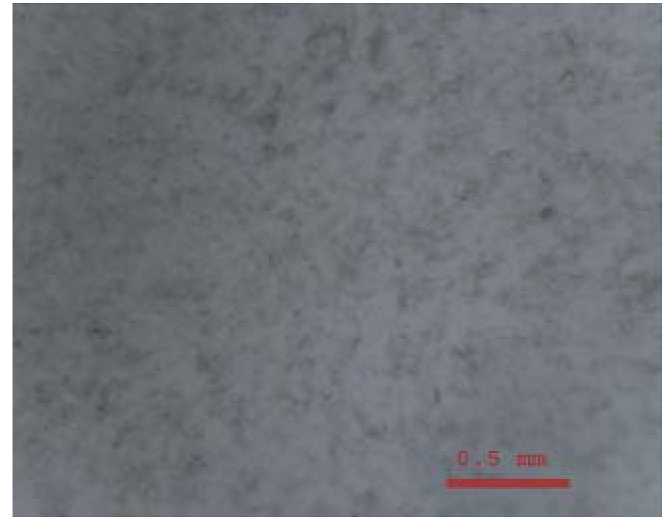
PICA manufacturing



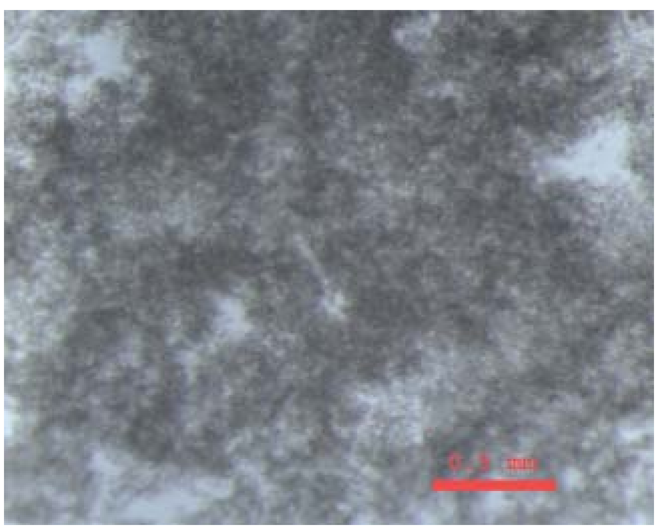
Optical microscopy



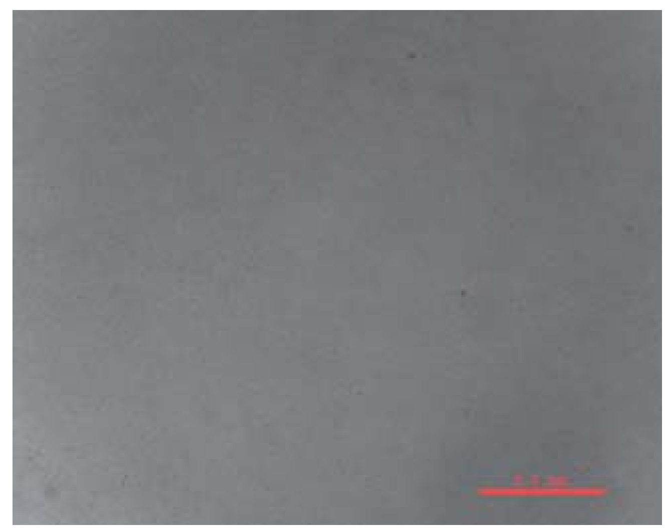
(**3**) Purified HiPco in EG/phenolic



(**1**) NT-Ph-$SO_3^-Na^+$ in EG / phenolic

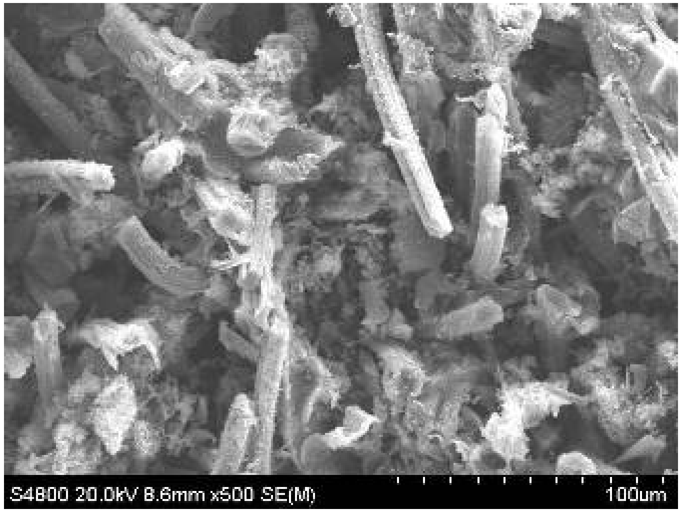


(**2**) NT-LP in EG / phenolic

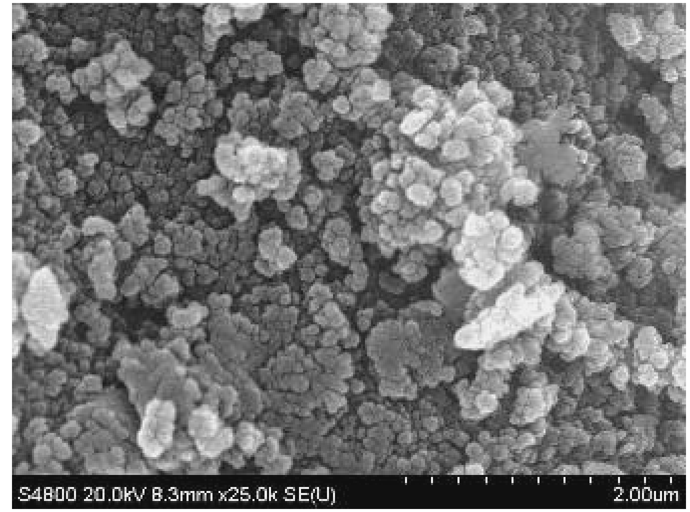


(**1**) NT-Ph-$SO3^-Na^+$ in EG / phenolic after vacuum outgassing (isopropyl alcohol removed)

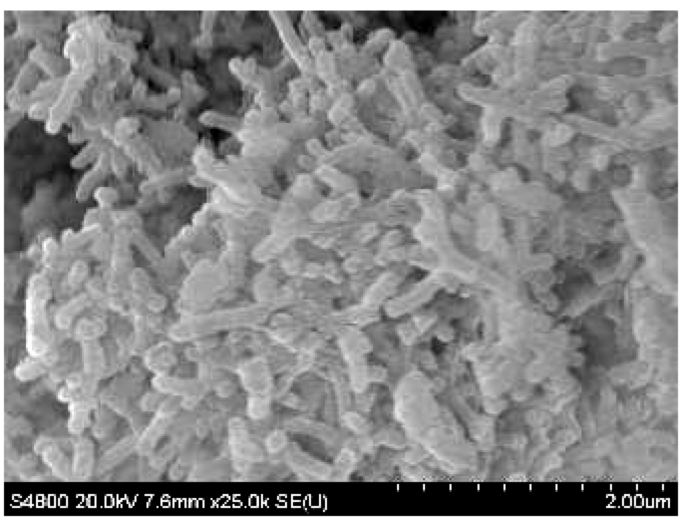
SEM



Typical low magnification image of PICA



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



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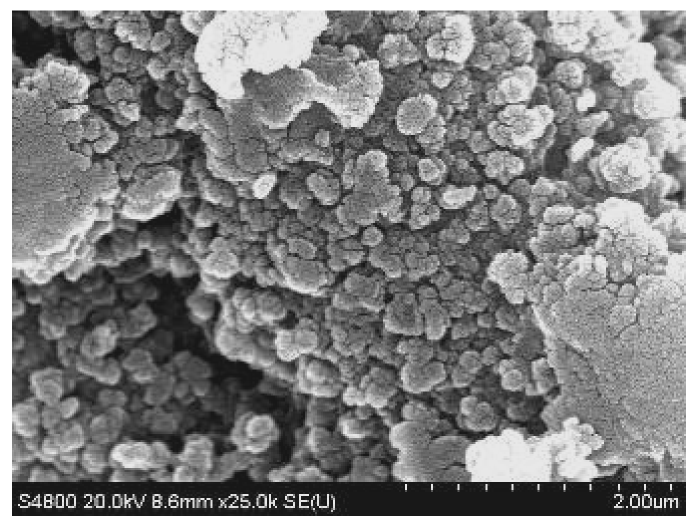
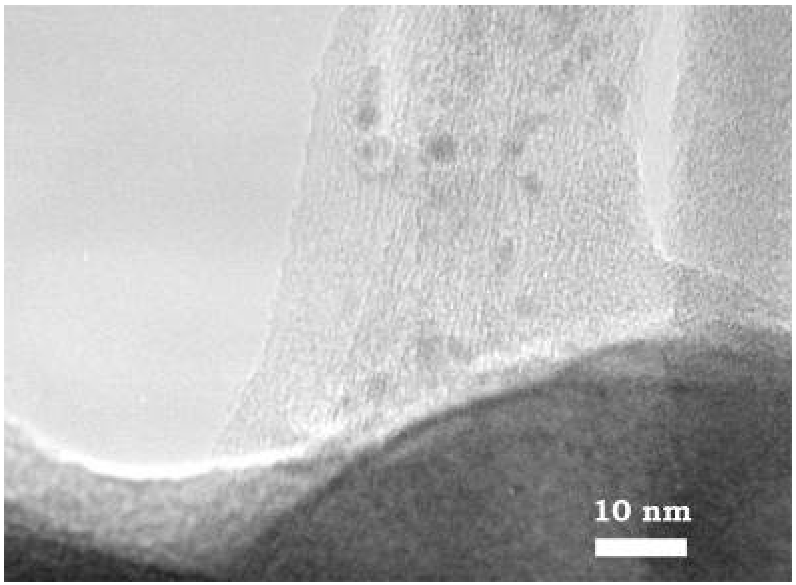
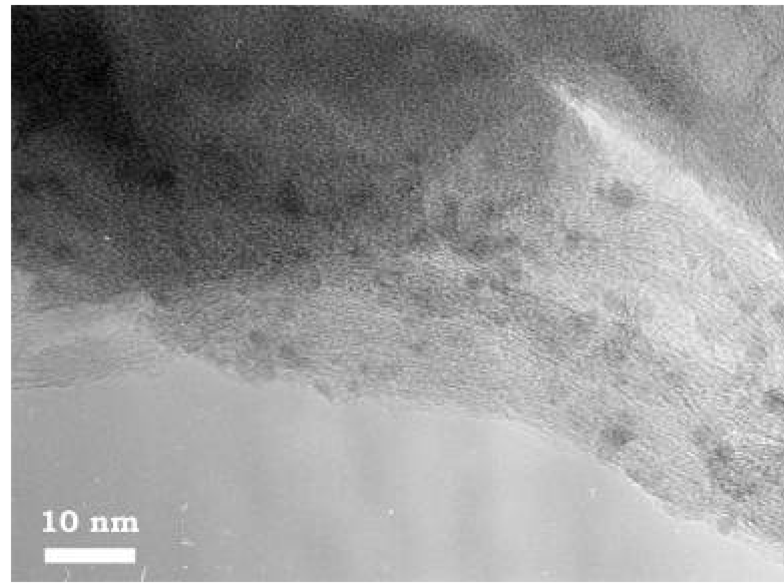


(**2**) NT-LP in PICA

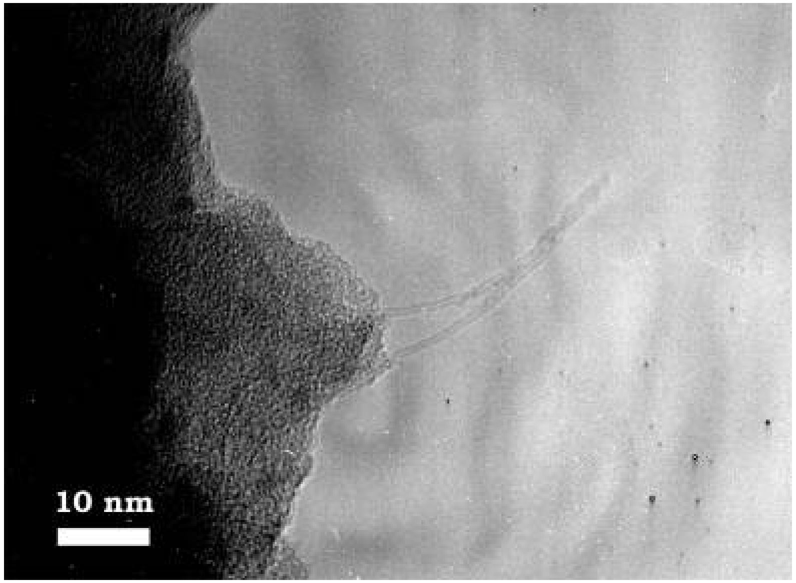
TEM

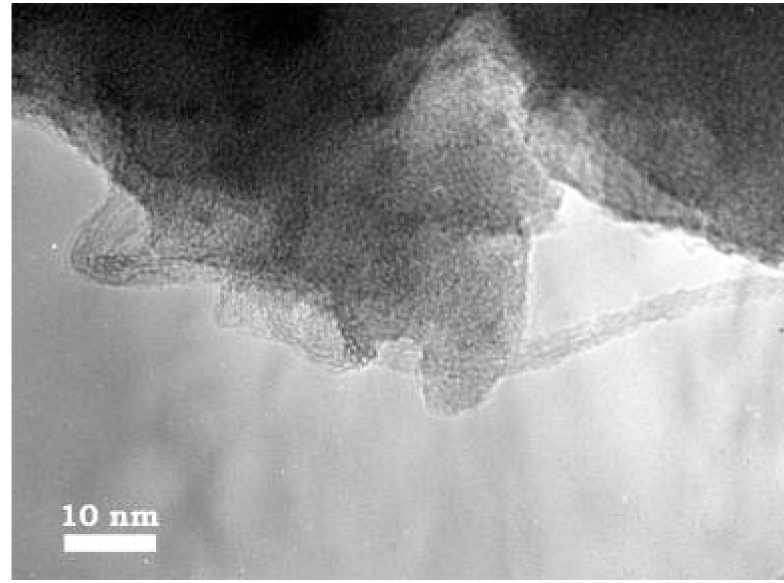


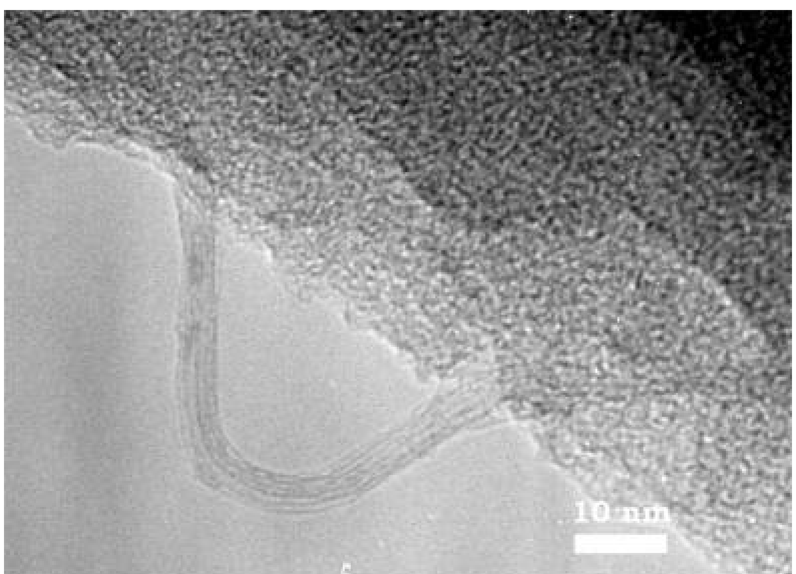


(**3**) Purified HiPco NT in PICA

TEM







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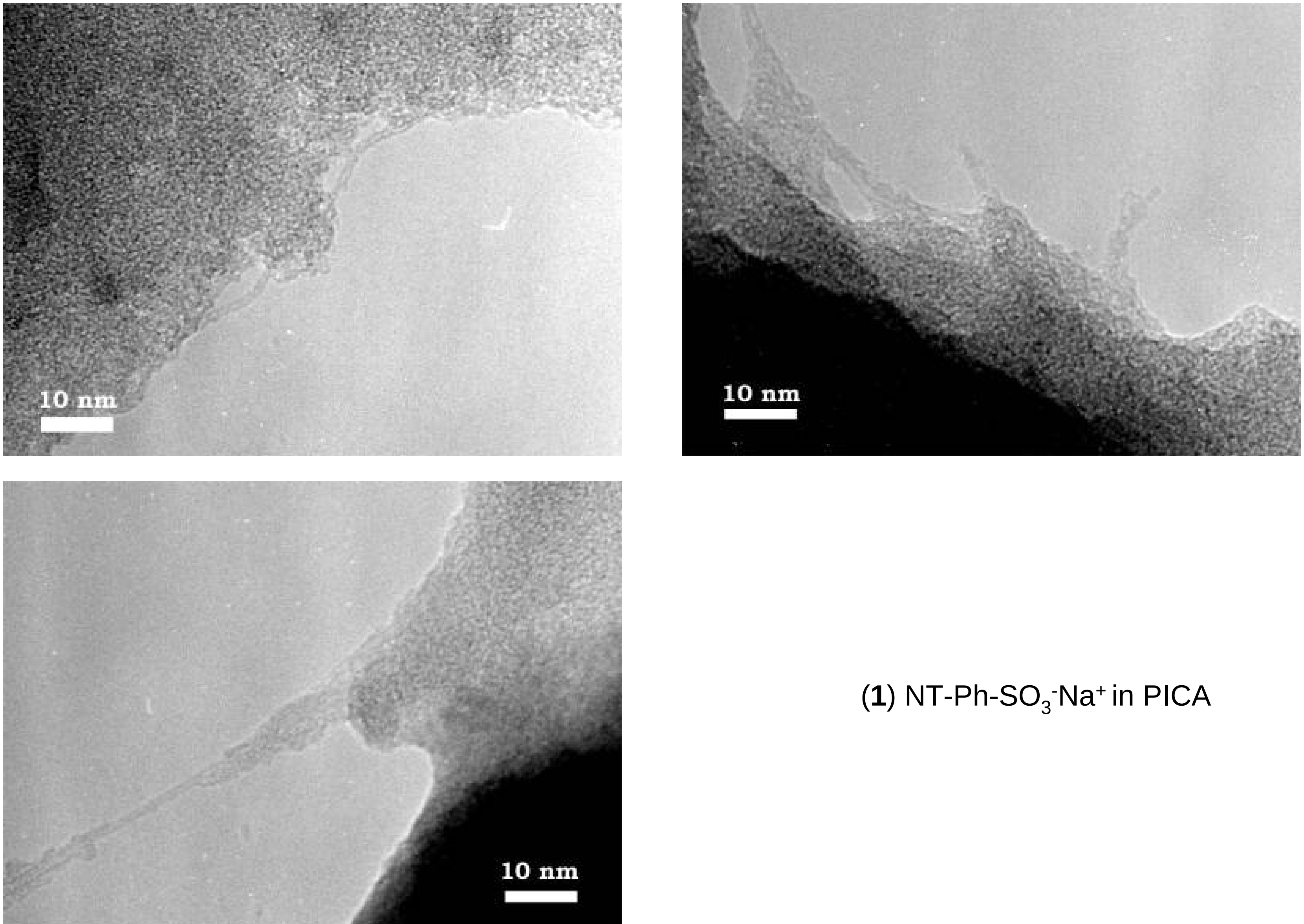
TEM



(**1**) NT-Ph-$SO_3^-Na^+$ in PICA

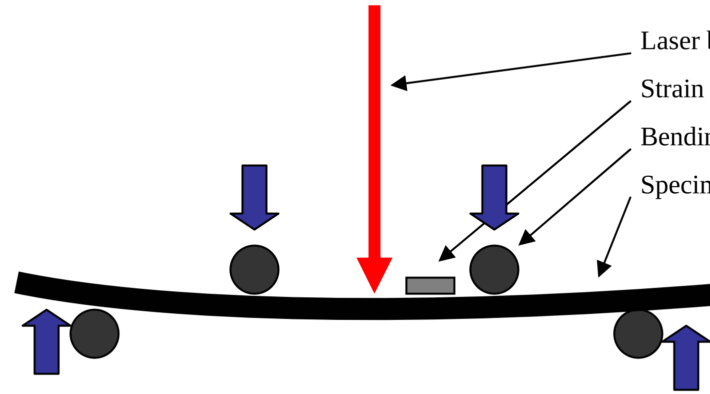
Raman load transfer test

NT Raman G+ frequency shifts under strain. Strain in the matrix is measured independently with strain gage
For chiral NTs (semiconducting)

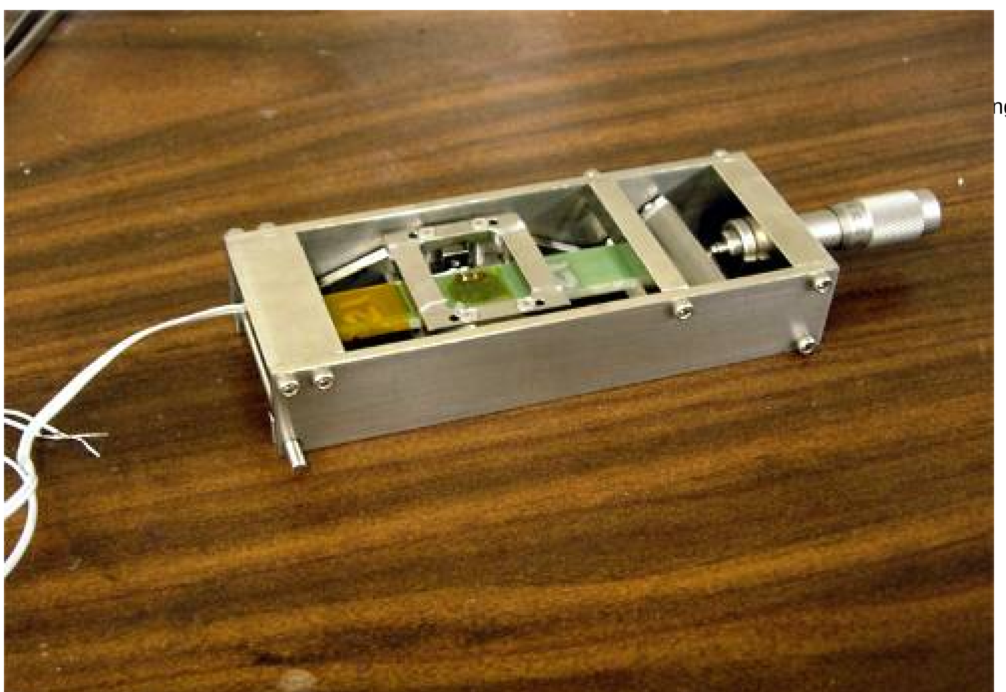
$$\Delta\omega / \omega_0 \approx -\gamma(1-\nu_t)\varepsilon_z ,$$

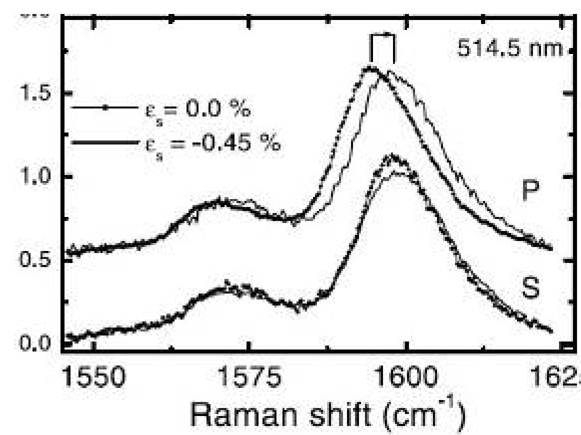
γ = ~1.24 - Grueneisen parameter
ν_t = ~0.19 - NT Poisson ratio
ε_z, ε_{ci} - strain along nanotube axis and circumference

S. Reich *et al.*, PRB **61**, 13389 (2000),
V. Hadjiev *et al., Applied Physics Letters*, Vol. 78, pp. 3193-5 (2001)
V.G. Hadjiev *et. al., Composites Science and Technology, 66, 1 ,pp 128-136* (2006)

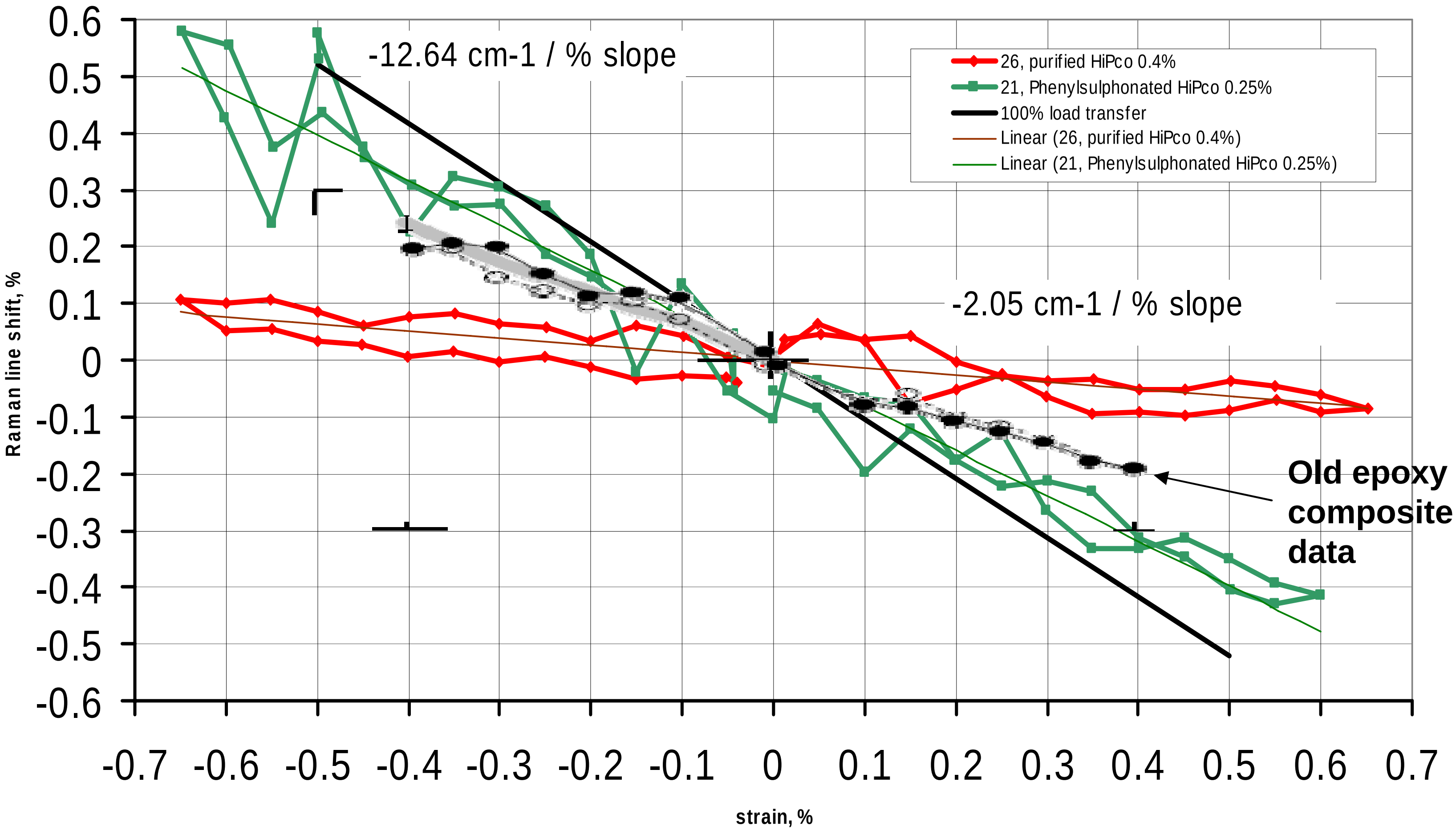


$$\varepsilon_z \ (\text{along } z), \quad \varepsilon_{ci} = -\nu_t \varepsilon_z \ (\text{circumference})$$





Raman line shift, % vs. strain



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-$SO_3^-Na^+$ - 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.