Processing and properties of aligned carbon nanotube /polymer matrix composites

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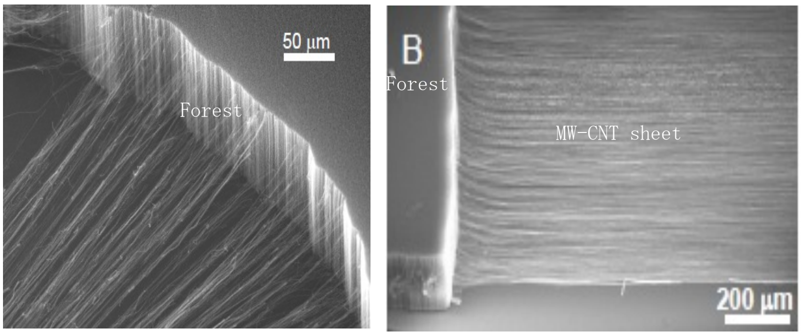
Outline

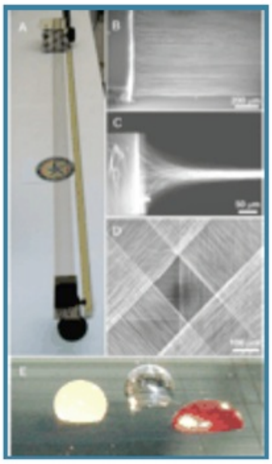
- Introduction
  - Previous work on aligned CNT/epoxy composites in our group
  - Objectives
- Damage progression behavior and strength
  - TEM observations of composites subjected to tensile stress
  - Critical CNT length and CNT strength
- Elastic modulus
  - CNT orientation angle distribution
  - Estimation of elastic modulus using Eshelby's theory
- Conclusion

Forest-drawn CNT sheet

The technology to produce horizontally aligned CNT sheets from a vertically aligned CNT forest was proposed in 2004.

The forest-drawn CNT sheets were particularly promising materials for use as a reinforcement of polymer because they are highly oriented, high volume fraction, and free-standing.

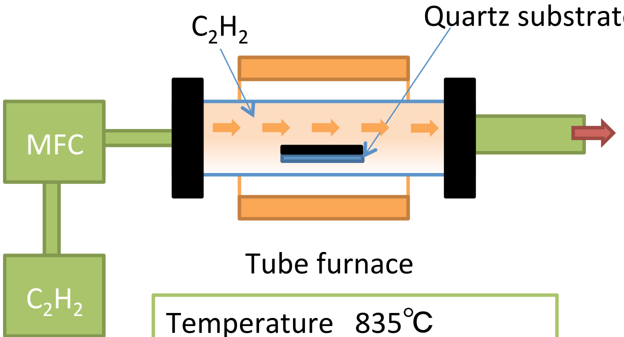




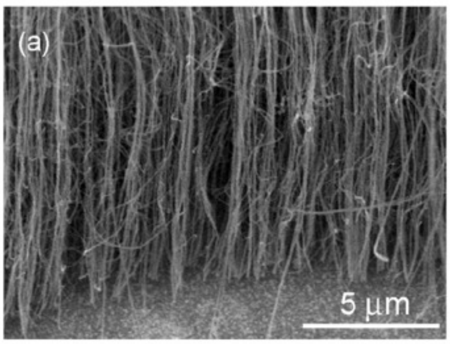
CNT-Forest and CNT-sheet
(M. Zang et al, University of Texas at Dallas, Science, 2004)

Synthesis method of CNT forest

A simple and efficient synthesis method for producing vertically aligned long MWCNTs was proposed by Prof. Inoue in 2008.
The MWCNTs with length exceeding 1 mm were grown on a bare quartz substrate using conventional thermal CVD with single gas flow (acetylene) for 20 min. Iron chloride powders are used as precursor of a catalyst .



Temperature 835℃
Pressure 10 Torr (1.3 kPa)
Flow rate (C_2H_2) 200 sccm
CVD duration 20 min!

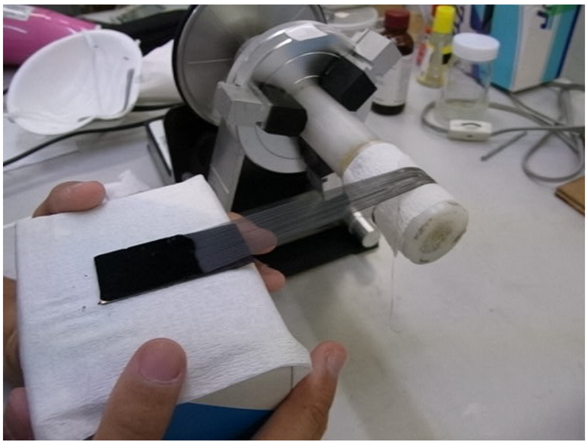


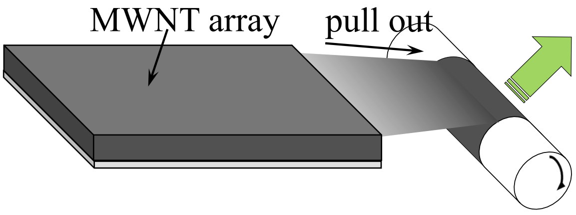
Inoue Y, Kakihata K, Hirono Y, Horie T, Ishida A, Mimura H., Appl Phys Lett 2008; 92 (21): 213113.

How to make forest-drawn CNT sheets

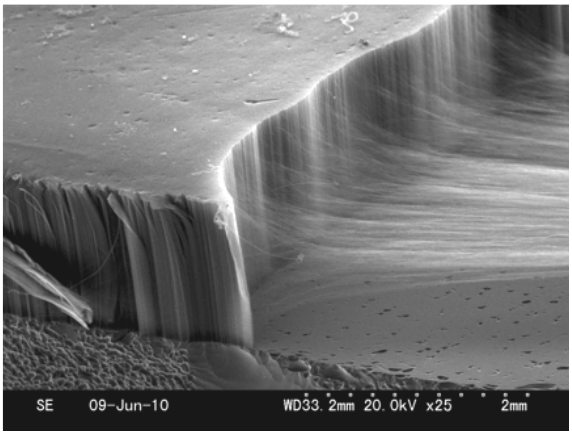
In addition to such a high growth rate, the CNT forest is spinnable.

Well-aligned MWCNT sheets are produced easily from the MWCNT forest by pulling it out to horizontal direction.

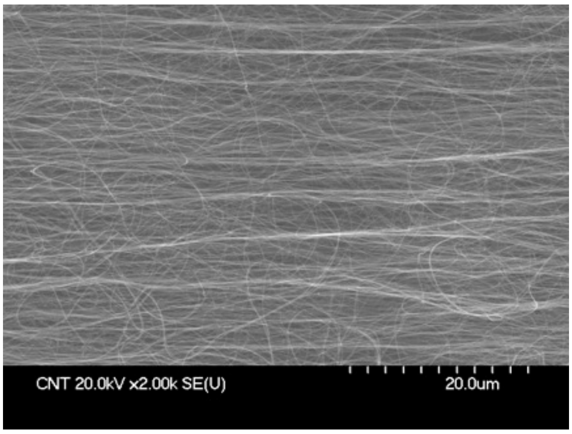




Scanning electron micrographs presenting CNT forest, and horizontally aligned CNT sheet



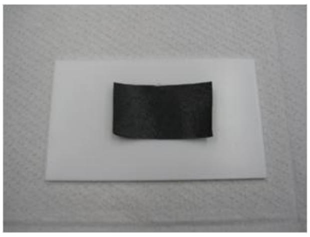
CNT forest



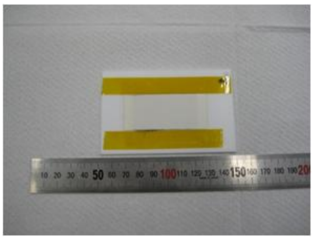
Horizontally aligned CNT sheet

- Diameter 50–70 nm, Length 1.3 mm, Aspect ratio > 10,000
- Most of the CNTs are aligned, waviness and entanglement are also visible. The CNT sheets are not perfectly aligned.

Processing of CNT/epoxy prepreg

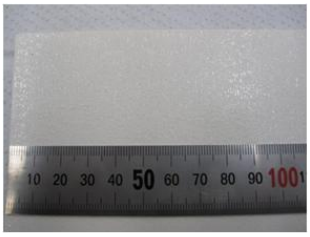


Stacked CNT sheet
(12.5 mm width, 45 mm length)



CNT sheet was put on a PTFE sheet and covered with epoxy resin film with release paper.

Resin impregnation
(90°C for 3 min)

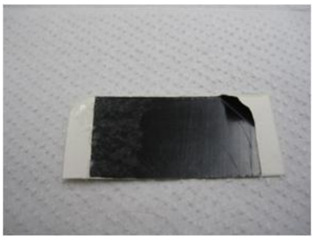


B-stage un-cured epoxy resin film with release paper (30g/m^2, 25μm)

Bisphenol-A type epoxy,novolac type epoxy, and an aromatic diamine curing agent

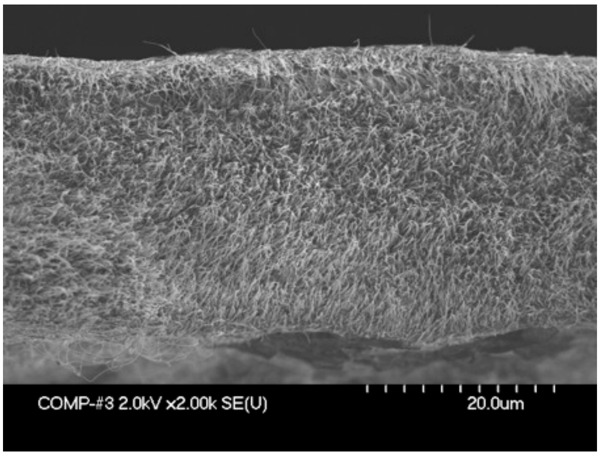
CNT/Epoxy prepreg had good drapability and tackiness.
CNT loading was well controlled by changing the CNT areal weight.

The prepreg sheet was cured at 130°C for 1.5 h between steel plates in an oven, yielding a film specimen.

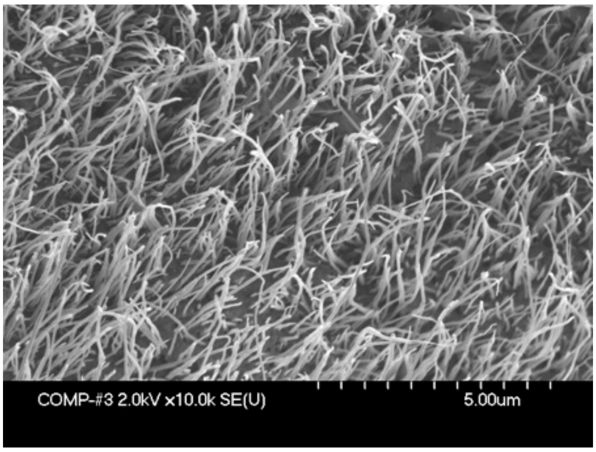


CNT/Epoxy prepreg

Fracture surfaces of CNT/epoxy composites



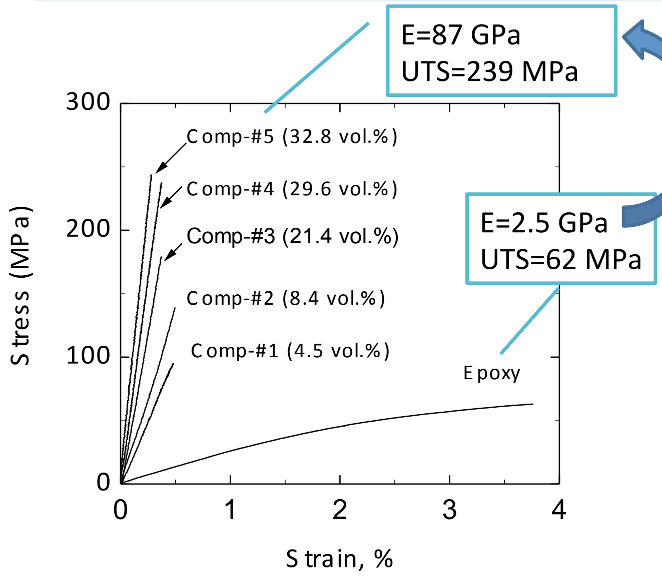
Comp #3, 21.4 vol.%



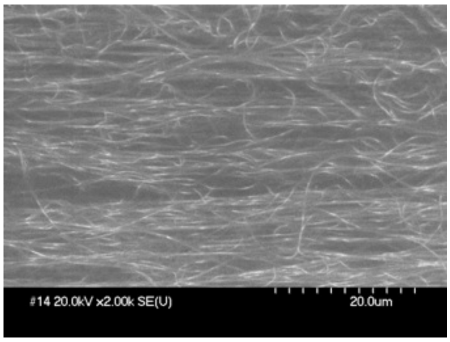
Comp #3, 21.4 vol.%

No visible void or resin-rich region was observed.
Epoxy resin is well penetrated between CNTs.
The SEM observations demonstrate that the prepreg process contributes to the high quality of the CNT/epoxy composites.

Stress / strain curves



CNT(32.8 vol.%) Composite
Young's modulus; 35-fold increase
Strength; 4-fold increase



Scanning electron micrographs of CNT/ epoxy composites (Comp-#3, 21.4 vol.%).

The composites exhibit much higher elastic modulus and UTS as compared with randomly oriented CNT composites.
Quantitative discussions on the elastic modulus and tensile strength of the CNT/ epoxy composites have not been carried out.

* T. Ogasawara et al, *Compos Sci Technol*, 71 2 (2011), pp. 73–78.

Objectives

- Observations of damage progression under tensile loading using a TEM
- Investigation of the effect of CNT orientation angle distribution on the elastic modulus (Young's modulus)

- The direction for improving the mechanical property in near future.

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  - Estimation of elastic modulus using Eshelby theory
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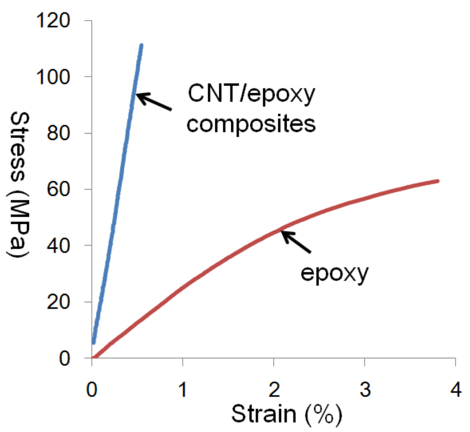
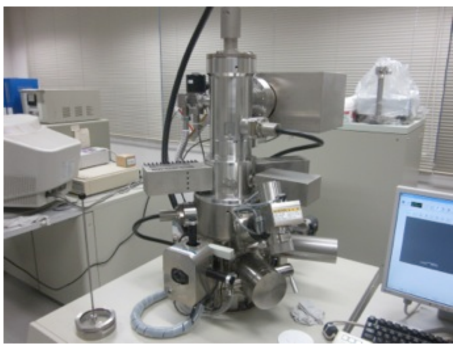
Nano-scopic damage observations

- Composite material
  - CNT (8 vol.%)/ Epoxy
  - Thickness 30 μm, E=20 GPa
- Tensile stress
  - 0, 45, 95, and 110 MPa



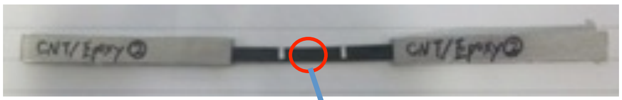
FE-TEM (JEM-2100F; JEOL, Japan)



FIB (JEM-9320; JEOL)

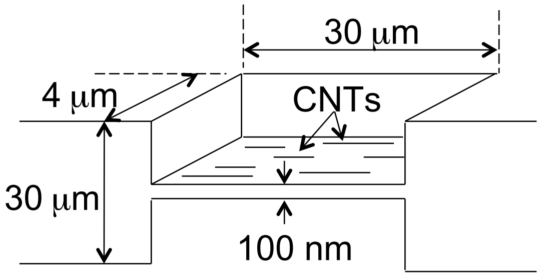
Sample preparation (FIB milling)

Tensile test specimen



5 mm X 1.5 mm

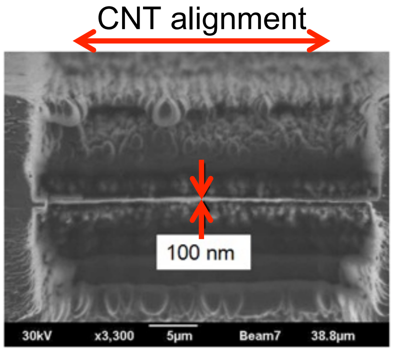
TEM tip-on holder



The machined area is approximately 30 μm wide, 4 μm deep, and 100 nm thick.

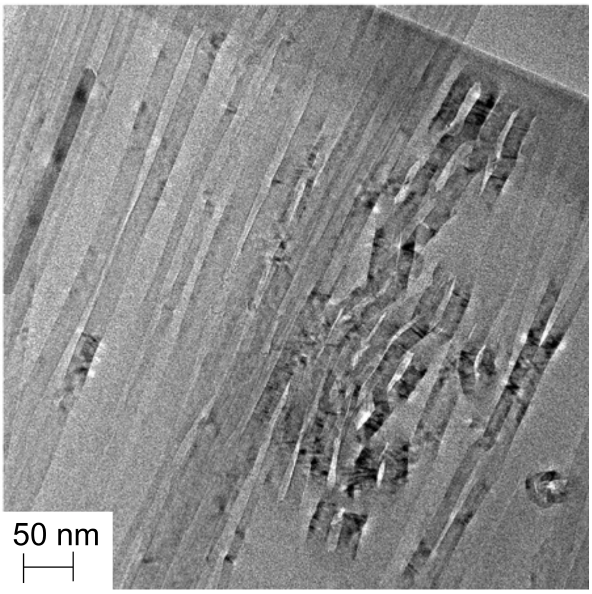
After tensile loading, each sample was cut into a rectangular piece (5 mm long, 1.5 mm wide) and set on a TEM tip-on holder.
Thin samples for TEM observations were prepared using an FIB.

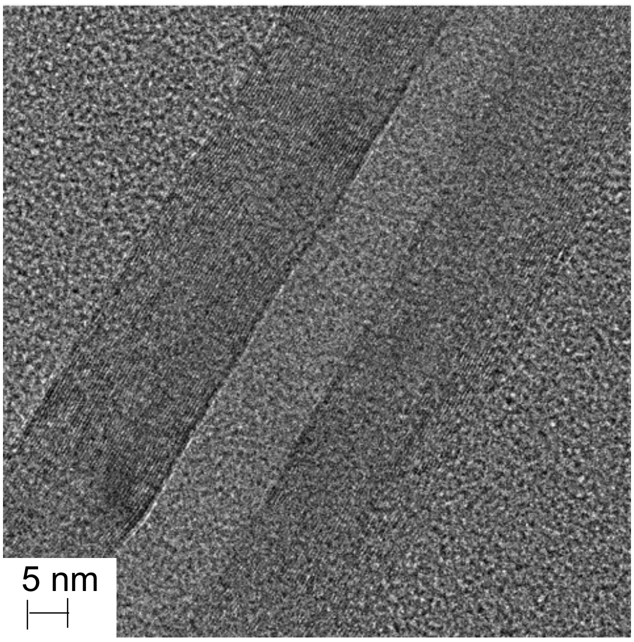
TEM observation area
2.8 x 3.5 μm, 12-15 /each specimen



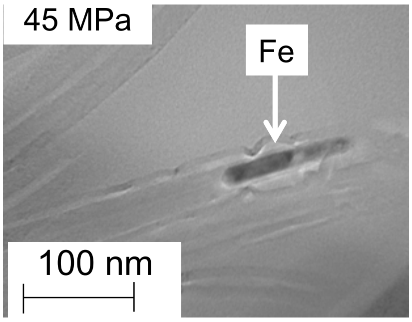
TEM observation sample (after FIB milling)

Damage progression (0 MPa)

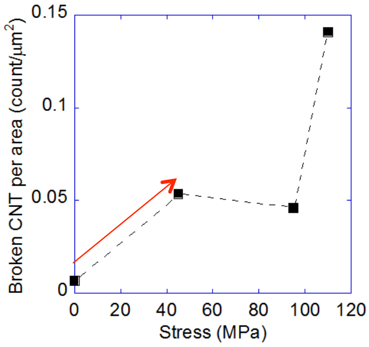




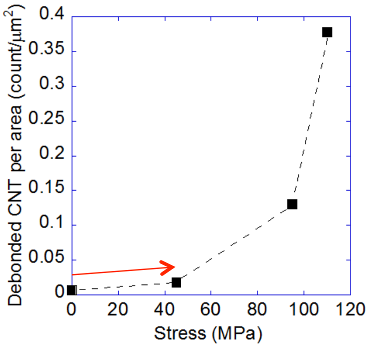
Damage progression (45 MPa)

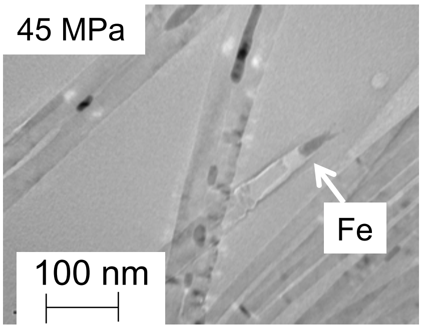


Number of CNT breaks



Number of debonding

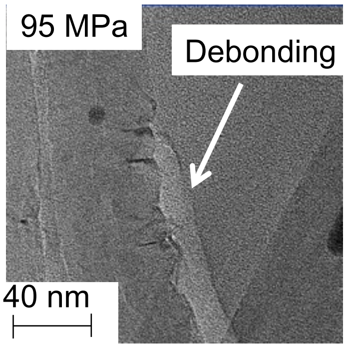




At the first loading step (0–45 MPa), the CNT breaks around metallic catalyst are mainly observed.

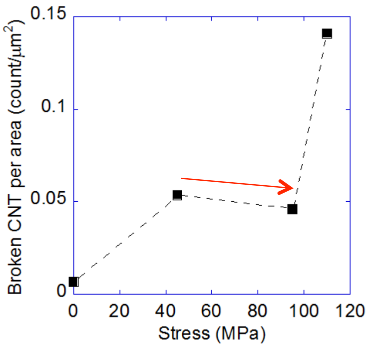
The CNT length is estimated to be 150-200μm, which is long enough as reinforcement.
The CNT breaks do not affect the composite tensile strength and elastic modulus.

Damage progression (95 MPa)

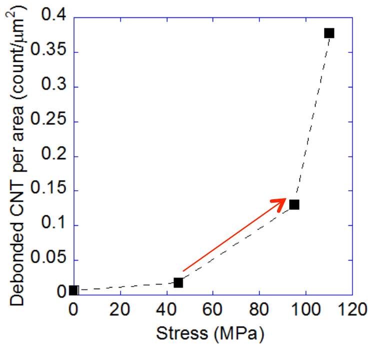


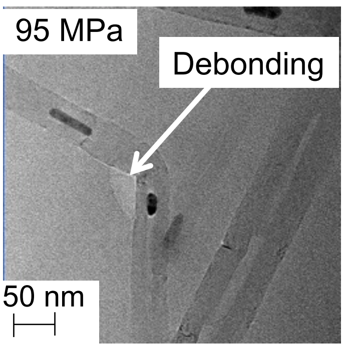
Bamboo like structures

Number of CNT breaks



Number of debonding

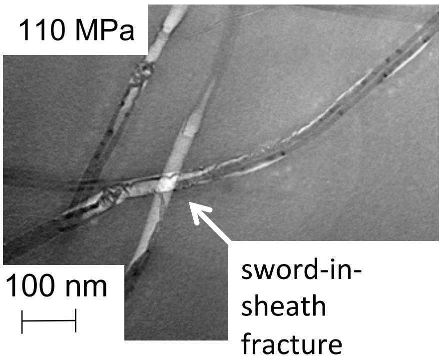




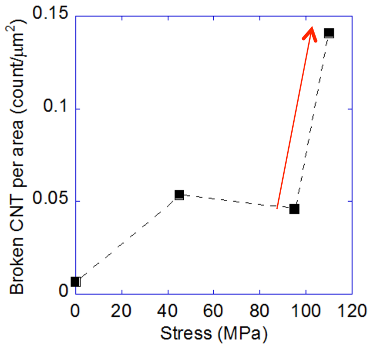
At the second loading step (45–95 MPa), interfacial debondings around abnormally grown structures are observed.
On the other hand, the fracture of CNTs never proceeded.

Debonding does not affect the mechanical properties significantly.

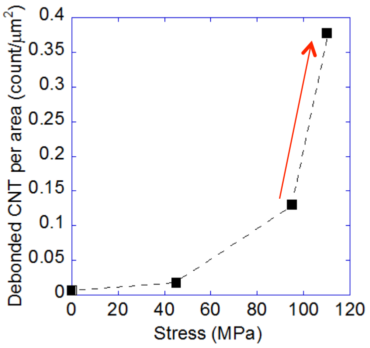
Damage progression (95-110 MPa)

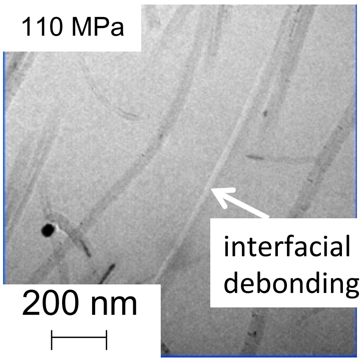


Number of CNT breaks



Number of debonding





At the final loading step (95–110 MPa), multiple failures of CNT in the matrix, and interfacial debonding along the ordered CNT are clearly observed.

Appearance of CNT failure is sword-in-sheath type. This suggests that the strength of the most outer layer is critical.

Critical length of CNT

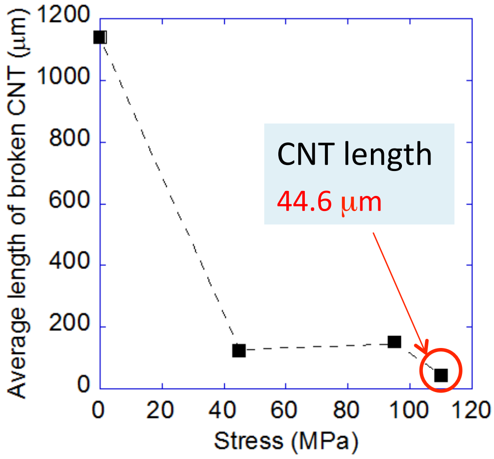
- TEM observation
  - Observed CNT length 1.12 mm
  - Number of CNT break (@ 110 MPa) 25

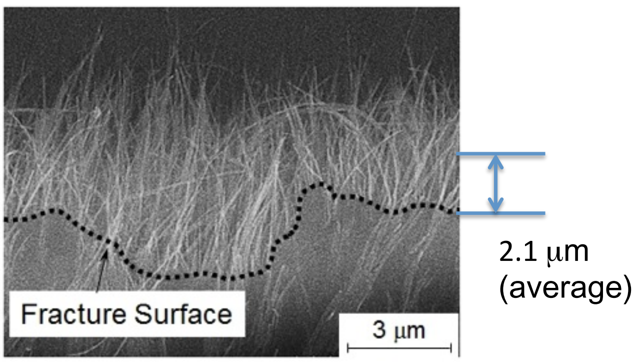
} CNT length 44.6 μm

- SEM observation (Pull-out length)
  - Pulled out length of CNT; 1.05 ~ 7.4 μm
  - Critical CNT length; 4.2 ~ 29.6 μm

} CNT length 16.4 μm (average)

$$L_{cr} = 4L_{exposed}$$





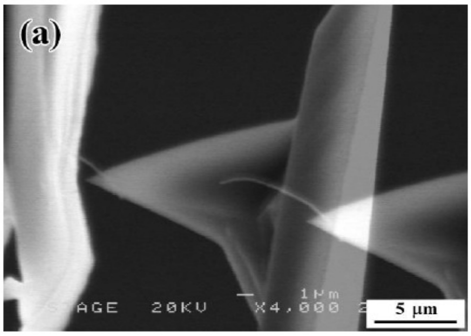
SEM photograph illustrating the fracture surface

CNT strength estimation

- Interfacial shear strength (IFSS) between CNT and epoxy (different composite system)
  - Pristine interface ~ 20 MPa
  - Debonded interface ~ 5 MPa

T. Tsuda, T. Ogasawara et al (2011)

$$\frac{L_{cr}}{2} = \frac{\sigma R}{2\tau}$$

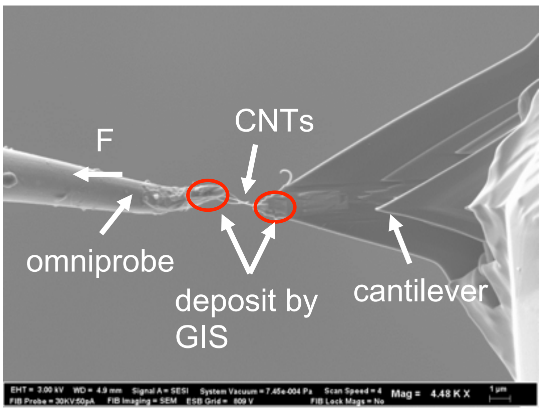


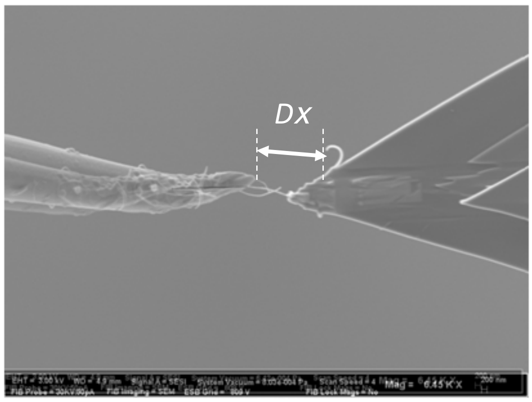
IFSS evaluation using nano-pullout method

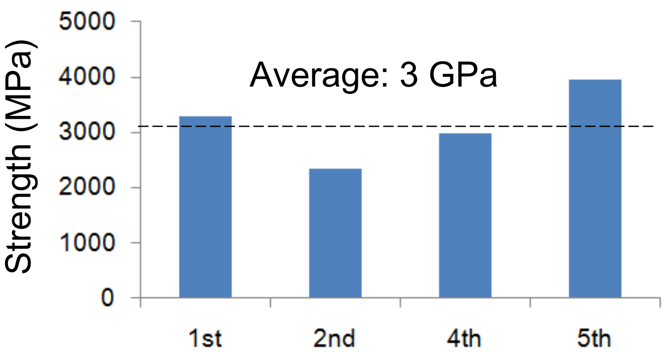
Estimated CNT strength

	Critical length (TEM) 44.6 μm	Critical length (SEM) 16.4 μm
Aspect ratio	900	330
Pristine interface (20MPa)	34.2 GPa	12.6 GPa
Debonded interface (5 MPa)	8.5 GPa	3.1 GPa

Tensile test of CNT







F = kΔx

σ= F/S

T. Tsuda and F. Deng, University of Delaware 2012

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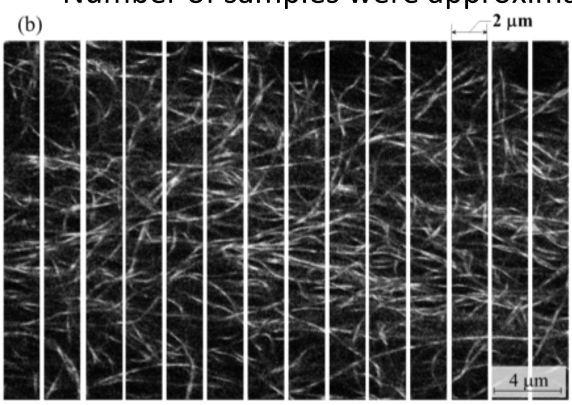
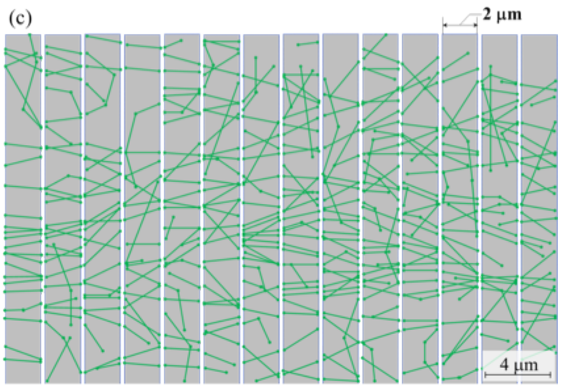
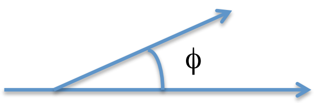
Evaluation of CNT orientation angle

- Composite material
  - CNT (13 vol.%)/ Epoxy , E=30 GPa
- Each SEM photograph was divided every 2 μm to material axis direction.
- Orientation angle of each CNT in the gauge length (2 μm) was measured.
- Number of samples were approximately 500.



SEM photograph

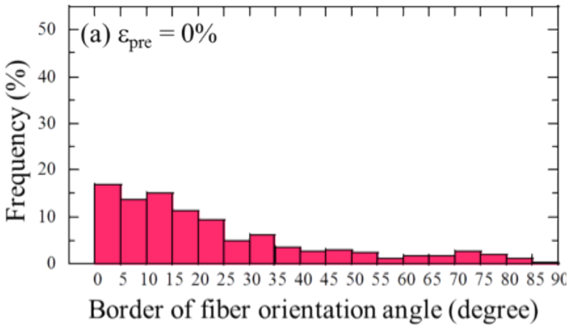


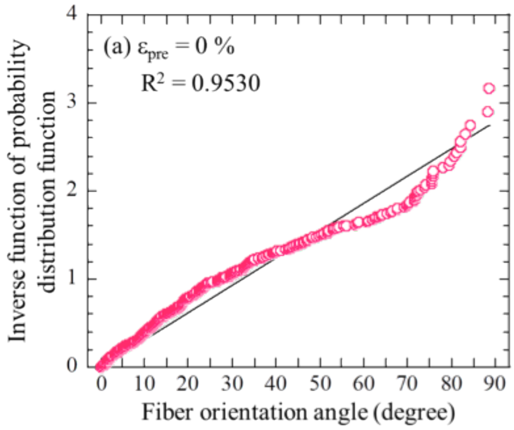


Material axis

Evaluation of CNT orientation angle

- Orientation angle is well fitted to normal distribution.
- The standard deviation; 31.8 deg.





Histogram of CNT orientation angle

Normal distribution plot

Eshelby, Mori-Tanaka theory

- Eshelby, Mori-Tanaka theory

$$\mathbf{D} = v_0\mathbf{D}_0 + \sum_{r=1} v_r\{\mathbf{D}_r\mathbf{A}_r\} = v_0\mathbf{D}_0 + \sum_{r=1} v_r\left\{\mathbf{D}_r\mathbf{A}_r^{di}\left(v_0\mathbf{I} + \sum_{r=1} v_r\left\{\mathbf{A}_r^{di}\right\}\right)\right\}$$

$$= v_0\mathbf{D}_0 + \sum_{r=1} v_r\left\{\mathbf{D}_r\mathbf{A}_r^{di}\right\}\left(v_0\mathbf{I} + \sum_{r=1} v_r\left\{\mathbf{A}_r^{di}\right\}\right)$$

$$\mathbf{A}_r^{di} = \left[\mathbf{I} + \mathbf{S}_0\mathbf{D}_0^{-1}(\mathbf{D}_r - \mathbf{D}_0)\right]^{-1}$$

- In-plane CNT orientation angle distribution (normal distribution)

$$\left\{D_{ijkl}\right\} = \int_\phi D_{mnpq}\, l_{mi}\, l_{nj}\, l_{pk}\, l_{ql}\, n(\phi)\, d\phi$$

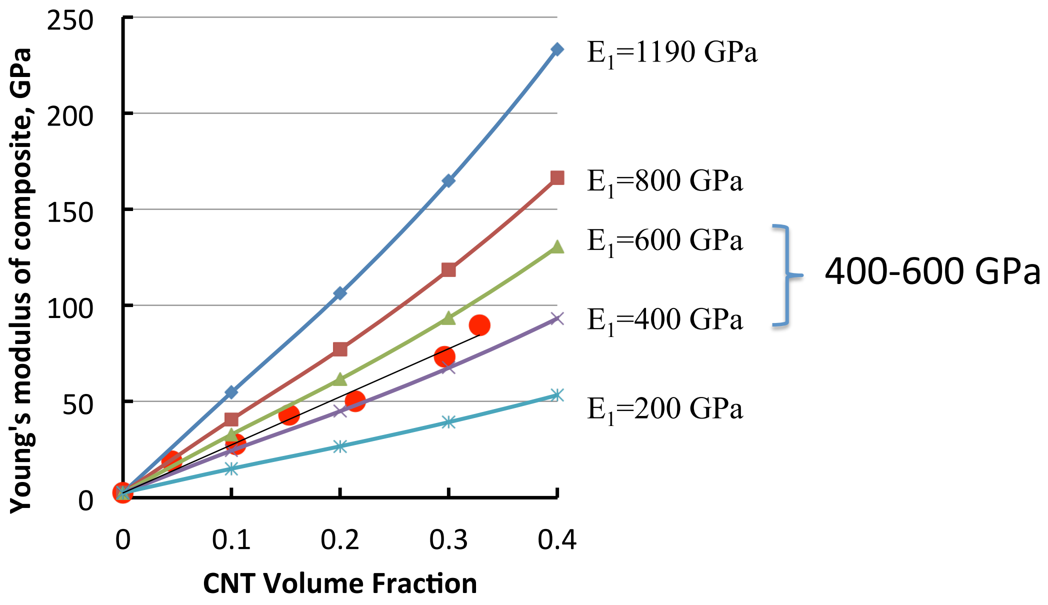
$$n(\phi) = \frac{1}{P(\sigma)}\exp\left(-\frac{\phi^2}{2\sigma^2}\right) \qquad P(\sigma) = \int_{-\pi}^{\pi}\exp\left(-\frac{\phi^2}{2\sigma^2}\right)d\phi$$

Notation
- D; Stiffness tensor
- S; Eshelby's tensor
- v; Volume fraction
- I; Unit tensor
- A; Concentration tensor
- n(f); Orientation distribution function (normal distribution)
- σ; Standard deviation of ϕ
- ϕ; Orientation angle
- l_{ij}; Angle transformation matrix

Subscript notation
- 0; matrix
- r; r-th component in matrix

Numerical results (1)
Effect of elastic modulus of CNT

- Aspect ratio; 300 (D=50 nm, L= 15 μm)
- Standard deviation of orientation angle distribution; 31.8 deg.



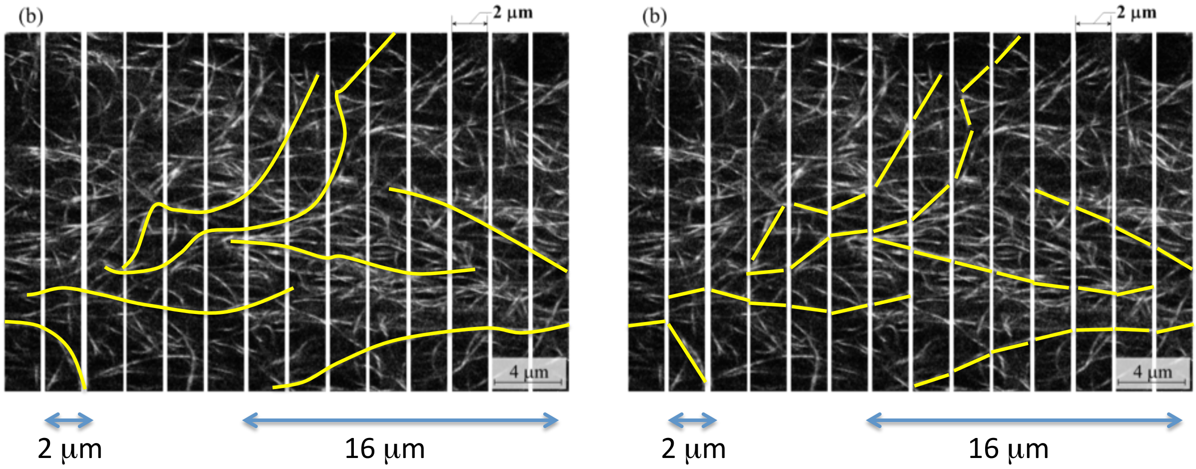
Young's modulus of MWCNT (Literature data)

Literature	Method	Young's modulus
Yu et al., Physical Review Letters 2000;84(24):5552–5	Dual AFM cantilevers	270-950 GPa
Demczyk et al., Materials Science and Engineering A334 (2002) 173–178	TEM direct tension	900 GPa
J.-P. Salvetat et al., Appl. Phys. A 69 (1999) 255.	AFM ends clamped	810 GPa
Xie et al., Journal of Physics and Chem- istry of Solids 2000;61(7): 1153–8.	AFM ends clamped	450 GPa
J.P. Lu: *Physical Review Letters*, **79** (1997), 1297-1300	MD calculation	1190 GPa

The Young's modulus of MWCNT; > 800 GPa

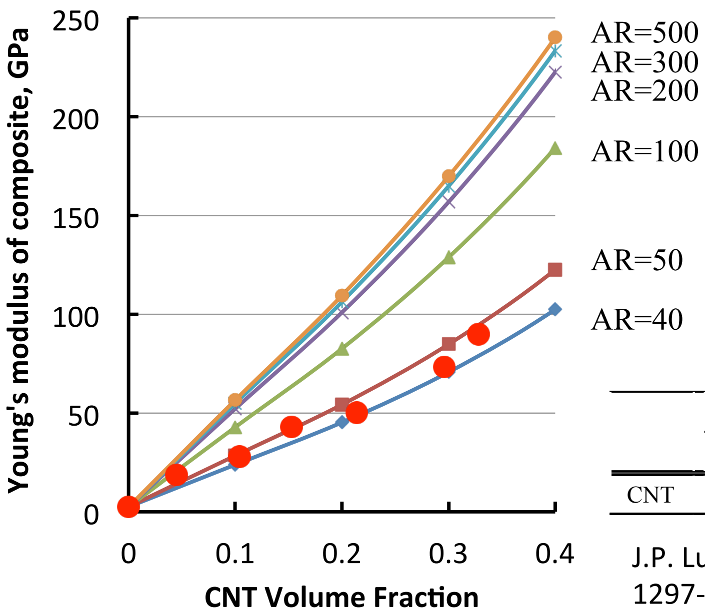
Effective CNT length

- All of the carbon nanotubes are not straight within the critical CNT length (16.4 μm)
- The CNT orientation angles were measured every 2 μm in this study.
- The effective CNT length for evaluating the elastic modulus should be 2 μm (aspect ratio of 50).



Numerical result (2) Effect of critical CNT length (aspect ratio)

- Young's modulus of MWCNT; 1.19 TPa (Lu et al, phy. Rev. Lett., 1997)
- Standard deviation of orientation angle distribution; 31.8 deg.

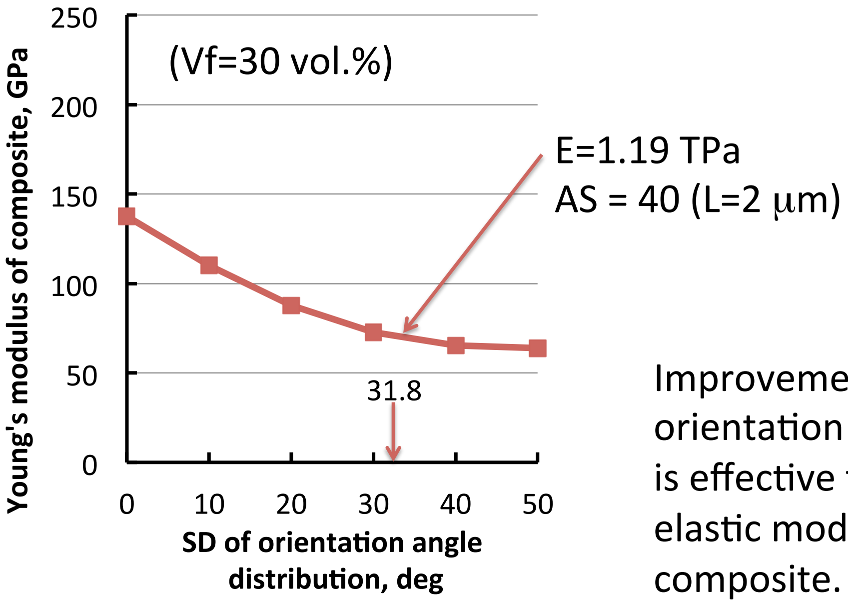


The best fit aspect ratio;
40 ~ 50 (L= 2 ~ 2.5 μm)

	Stiffness (GPa)			Posisson's ratio	
	E_1	E_2	G_{12}	ν_{12}	ν_{23}
CNT	1190	410	540	0.28	0.28

J.P. Lu: *Physical Review Letters*, **79** (1997), 1297-1300

Numerical result (3)
Effect of orientation angle distribution



Improvement of CNT orientation angle scattering is effective to increase the elastic modulus of composite.

70 GPa → 140 GPa !?

Conclusion

- Multiple CNT breaks and interfacial debondings were clearly observed under tensile load before the final failure.
- Critical CNT length was estimated to be approximately 16 μm from pullout length, and 45 μm from direct TEM observation.
- The strength of CNT/epoxy composites was mainly determined by tensile strength of the most outer layer.
- The strength of the CNT was estimated as 3-13 GPa using the critical CNT length (16 μm) and the IFSS (5-20 MPa).
- The Young's modulus of the CNT/epoxy composites was strongly affected by CNT orientation angle distribution.
- The estimated Young's modulus of CNT is approximately 1 TPa using the effective gauge length (2 μm) and the standard deviation of orientation angle distribution (31.8 deg).