BFRL

Predictions of the Thermodynamic Stabilities of Polymer/CNT Composites

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What is the problem?

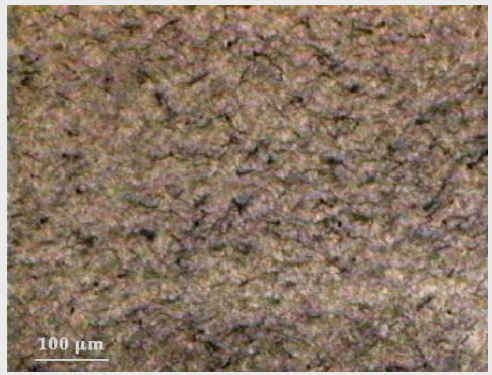
The potential of creating a new generation of commodity building materials by incorporating nanoscale additives into polymers is one of the most exciting prospects in nanotechnology. The ability to manufacture nanocomposite materials with good flammability performance and service life would enable US industry to maintain its leadership in current market and open new opportunities in construction and transportations sectors.

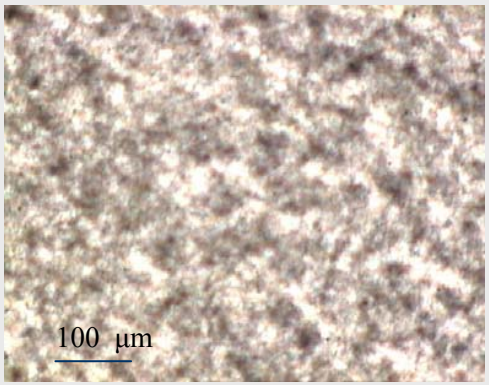
Unfortunately, nanostructured materials, such as carbon nanotubes (CNTs) and aluminosilicate clays, are not fully compatible with most hydrocarbon polymers and composites made by mixing them are actually colloidal suspensions that can lose their properties over time.

As a consequence, the service lifetimes of products made from these materials may be compromised. Moreover, the widespread use of products made from nanocomposites may pose significant health and environmental risks if the nanoadditives that they contain are released as a result of thermal or environmental degradation.

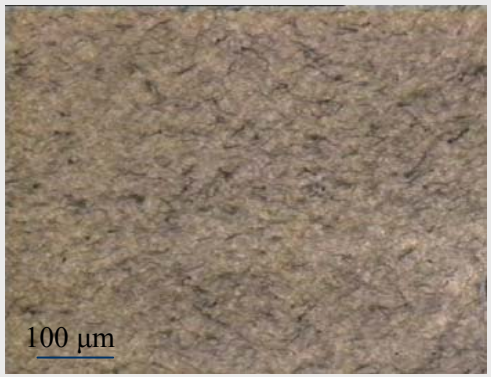
Shear induced flocculation

After waiting for 1hour without applying shear

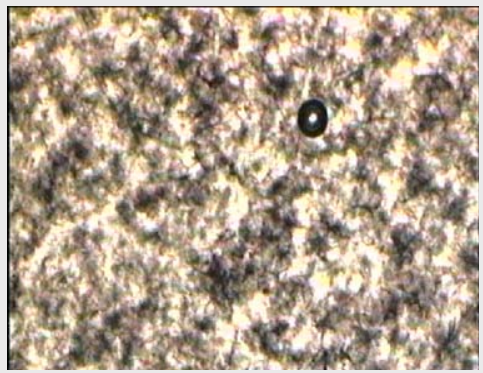




Before Shear



After shear (1000 s^{-1})



After applying low shear rate

wt % of MWCNTs = 0. 35

Rahatekar *et al.*, Journal of Rheology, **50**(5), 599-610 (2006)

Carbon Nanotube (CNT) Dispersion and Flammability

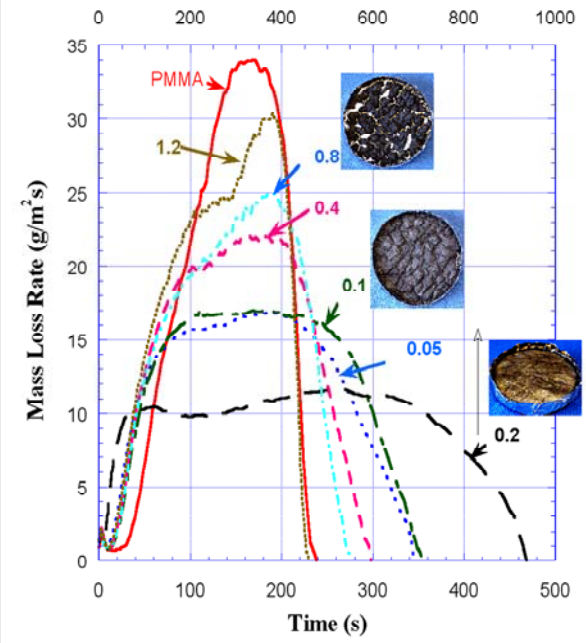
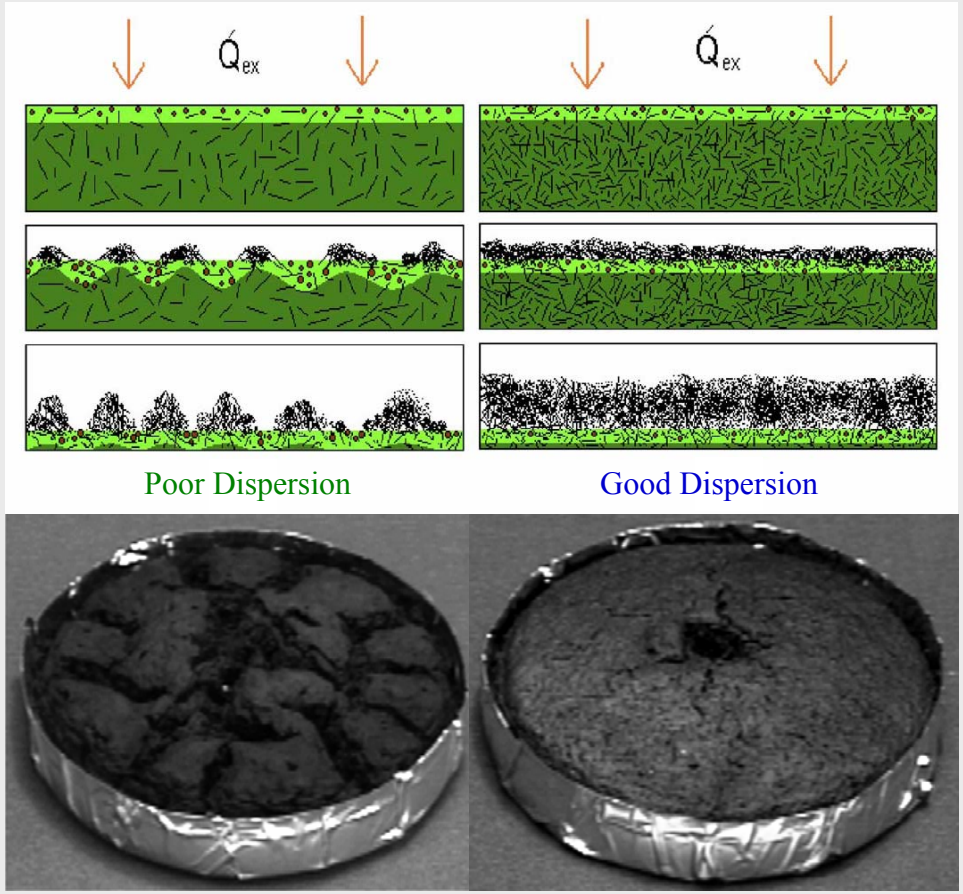


Figure 11. Mass loss rate curves of PMMA/SWNT(0.5 %) nanocomposites prepared with various concentrations of SWNT in DMF (mg/ml). All samples were 4 mm thick except 8 mm thick for 0. 2 mg/ml. Tests were conducted at 50 kW/m^2 in a nitrogen atmosphere.



Kashiwagi T. et. al. *Flammability Properties of Polymer Nanocomposites with Single-Walled Carbon Nanotubes: Effects of Nanotube Dispersion and Concentration;* Polymer; 46 (2005); 471–481.

NIST WSR-PFR (Sam Manzello)

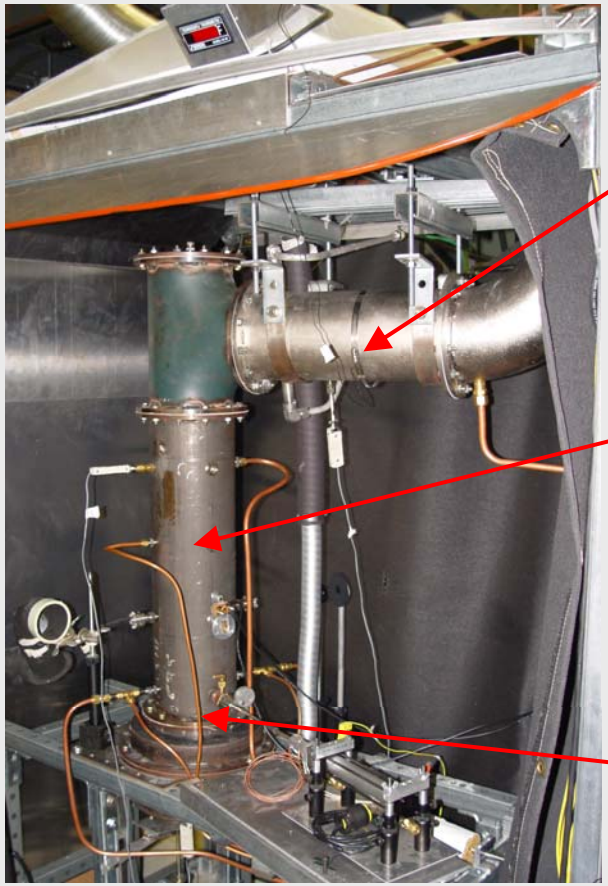
Combustion synthesis of nanostructures

- Reproducible method for generating the extreme conditions necessary for the formation of diverse nanostructures
- High-throughput. Generates several hundred grams of nanostructure product per hour
- Low cost. Use of combustion to engineer and produce nanostructures
- Facility well instrumented to characterize nanostructures produced

Design of WSR-PFR

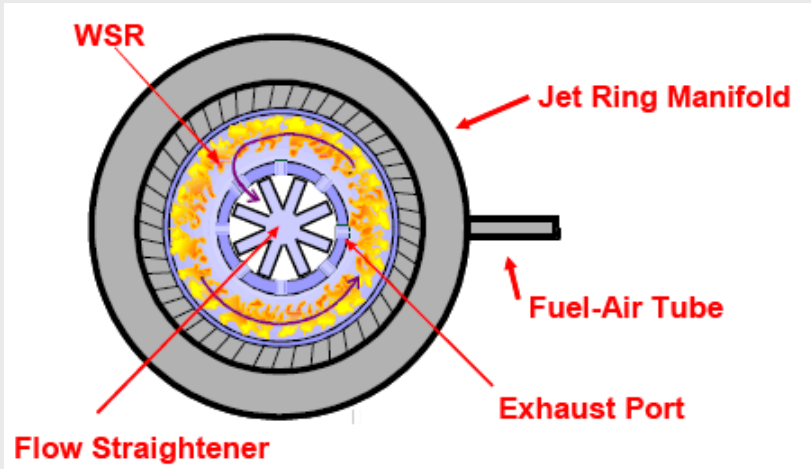
WSR Residence Times: 5 to 12 ms

WSR Volume:250 ml
PFR Reactor ID: 4.5 cm
PFR Length: 40 cm

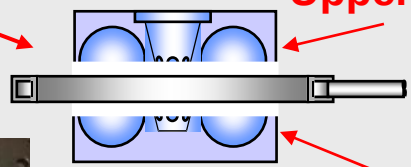


Afterburner

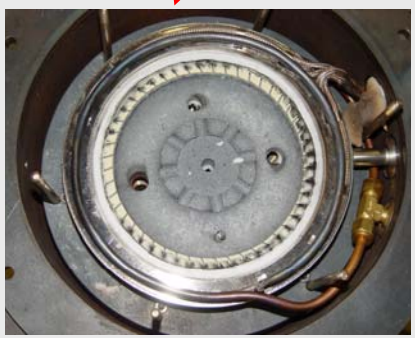
PFR
w/insulation



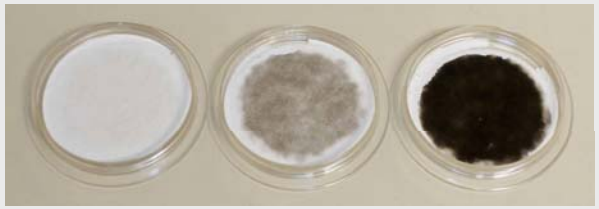
Jet Ring
Manifold



WSR



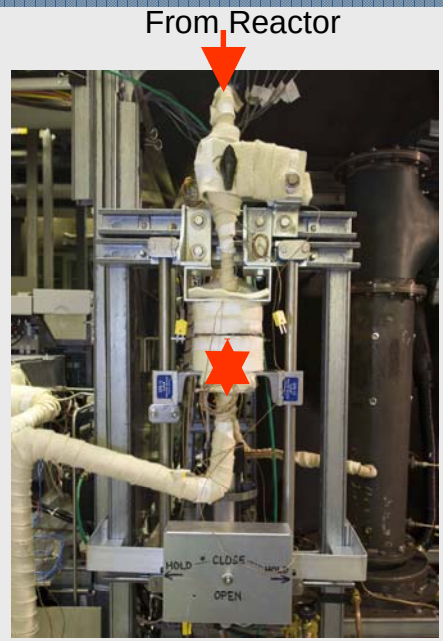
Experimental Materials



Φ = 1.85
30 min

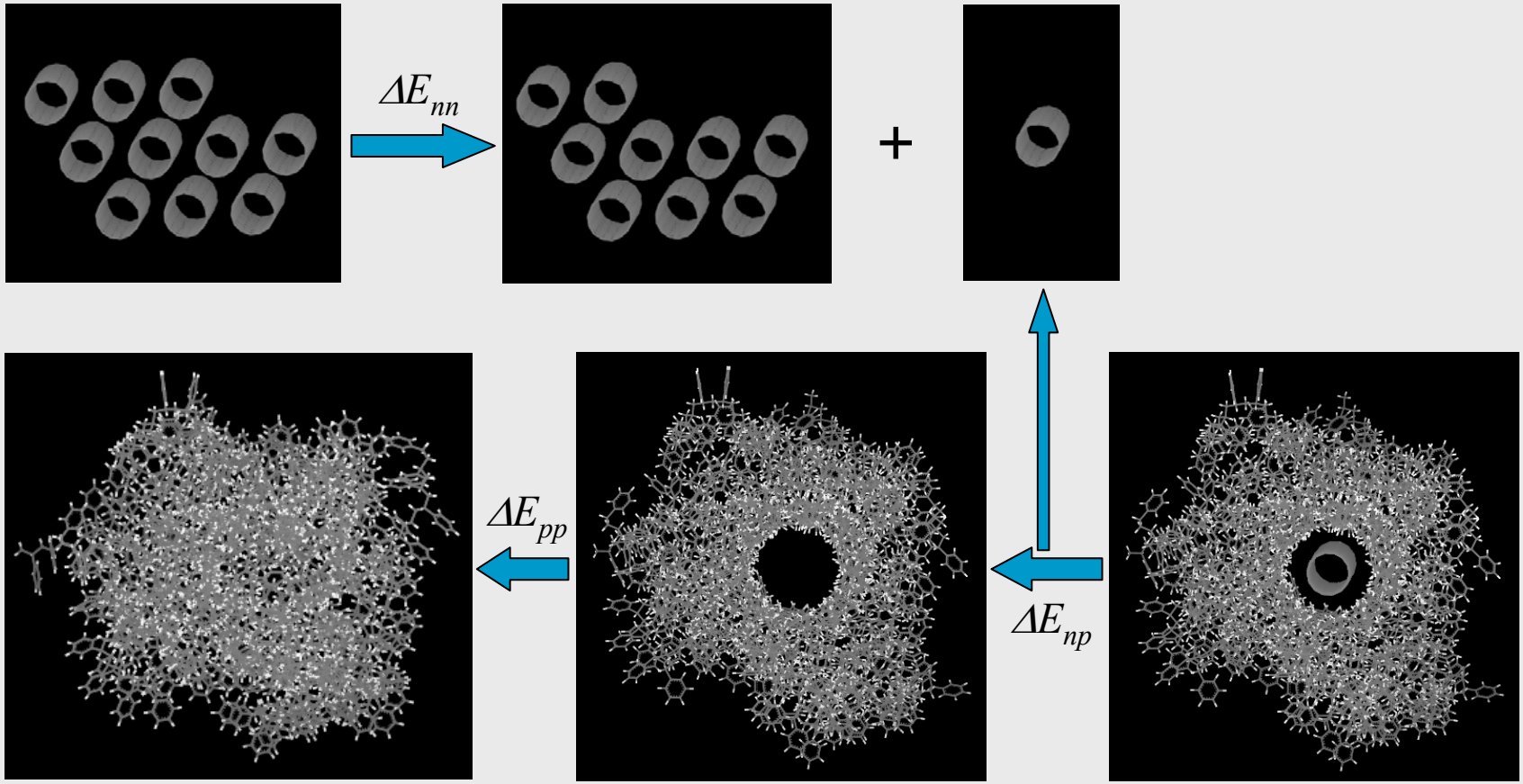
Φ = 2.0
5 min

Φ = 2.1
5 min



PS Resin	Solvent	Conc. of Resin in Soln'n (%)	Conc. of Nanoadditive in Soln'n (%)	Residual Mass Fraction* (%)	Color of Film	T_{max}** (°C)
Styron 663	MEK	10	0	1.0	Clear	397
Styron 663	DMF	10	0.5	0.7	Patches of Grey	403
Styron 663	MC	10	0.5	2.5	Black	417
Styron 663	MEK	10	0.5	1.3	Black	420
Styron 666	MEK	10	0	0.8	Clear	394
Styron 666	MEK	10	0.5	1.7	Black	423

Model of Formation of Polymer-CNT Composite



$$\Delta E_{mix} = \left[\Delta E^{S}_{nn} - \left(\Delta E^{S}_{np} + \Delta E^{S}_{pp}\right)\right] S$$

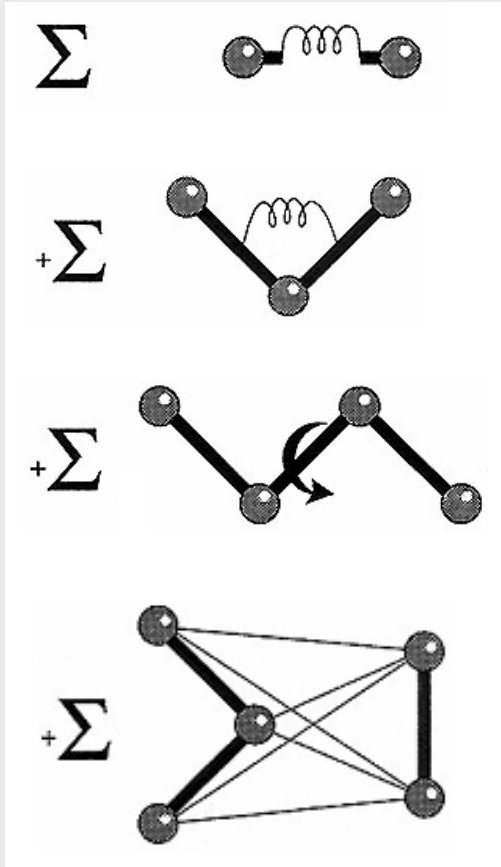
Molecular Mechanics (MM)

$$E_{bond} = k_r[r - r_e]^2$$

$$E_{angle} = k_\theta(\theta - \theta_e)^2$$

$$E_{torsion} = k_\phi[1 + \cos(n\phi - \phi_e)]$$

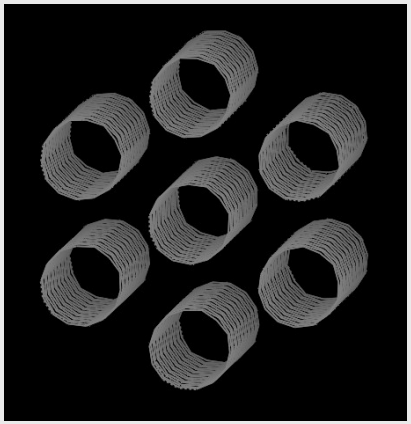
$$E_{nonbond} = \frac{A}{r^9} - \frac{B}{r^6} + \frac{q_i q_j}{\varepsilon r}$$



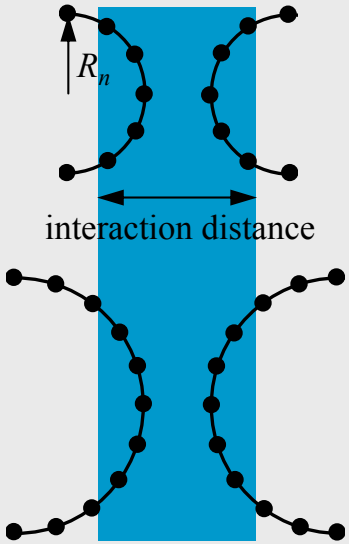
In MM calculations, thermodynamically stable structures for molecules and nanostructures are obtained as minimum energy points on the multi-dimensional surface that represents the potential energy as a function of the atomic coordinates. The potential energy is represented by a set of analytical functions, referred to collectively as a force field.

Nanotube-Nanotube Interaction Energies (ΔE_{nn})

Models of CNT Bundles Obtained using MM+ Force Field (by HyperChem)

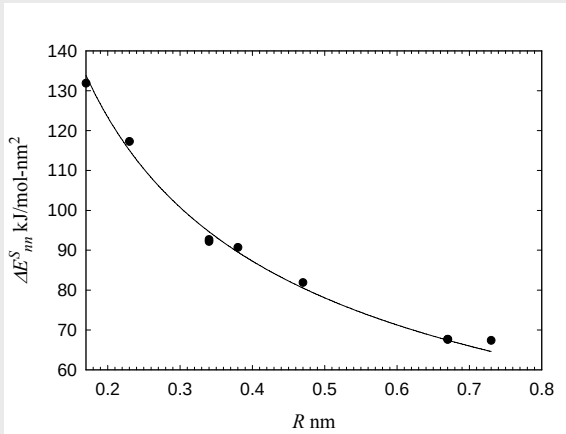


Chiral Indices	Nanotube Radius (nm)	Nanotube Length (nm)	Number of Nanotubes in the Bundle	ΔE^{S}_{nn} (kJ mol^{-1}nm^{-2})
3_2	0.17	3.80	7	131.9
6_0	0.23	3.78	7	117.3
5_5	0.34	3.39	7	92.7
6_4	0.34	3.90	7	92.2
10_0	0.38	3.78	7	90.7
7_7	0.47	3.88	7	81.9
10_10	0.67	3.39	7	67.7
12_8	0.67	3.90	7	67.6
20_0	0.73	3.78	7	67.4



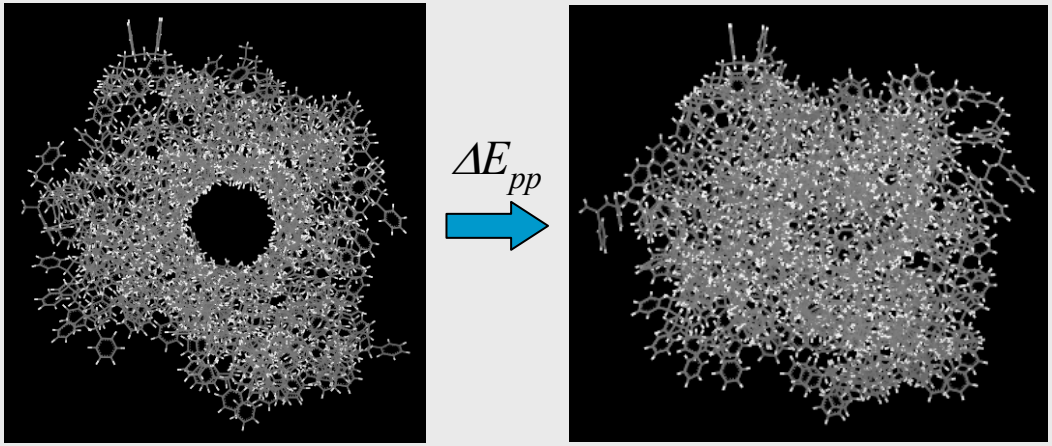
$$\Delta E^{S}_{nn} = \frac{C_{nn}}{\sqrt{R_n}}$$

$$C_{nn} = 55.2\, kJmol^{-1}nm^{-2}$$



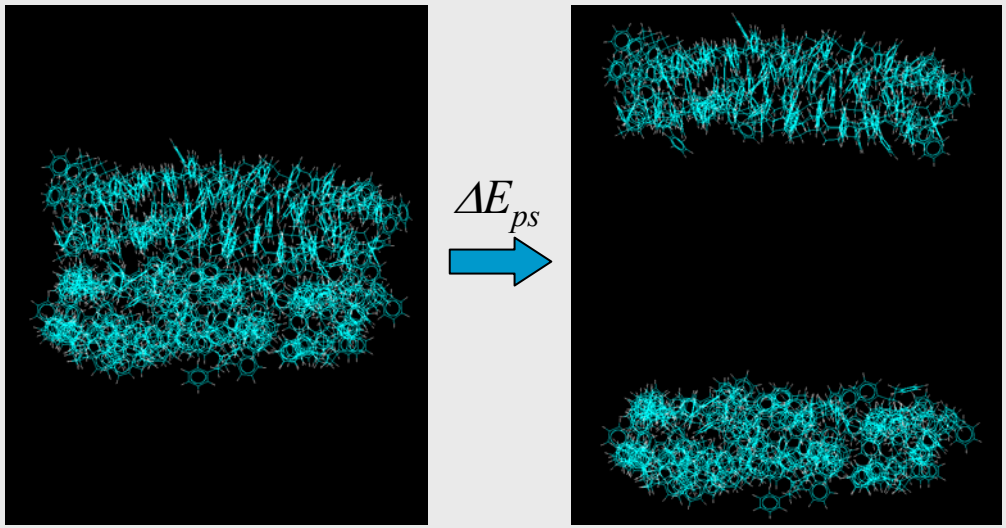
Tersoff J. and Ruoff R. S. *Structural Properties of a Carbon-Nanotube Crystal*; Phys. Rev. Lett.; 73 (1994), 676-679.

Polymer-Polymer Interaction Energies (ΔE_{pp})



$$\Delta E^{S}_{pp}(R) = \frac{-\gamma_{pp} 2\pi(R+d)l}{2\pi Rl}$$

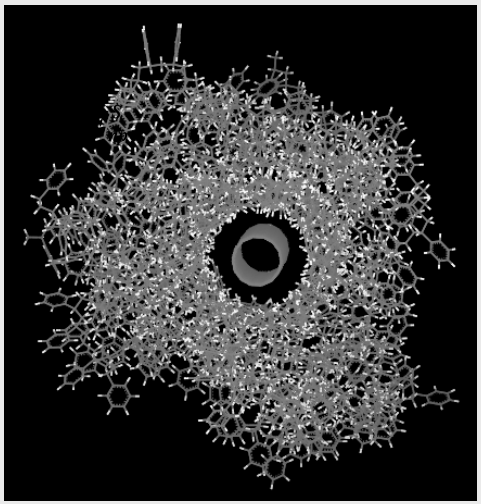
$$\Delta E^{S}_{pp}(R) = -\gamma_{pp}(1+\frac{d}{R})$$



γ_{pp} = 39.6 kJmol^{-1}nm^{-2}

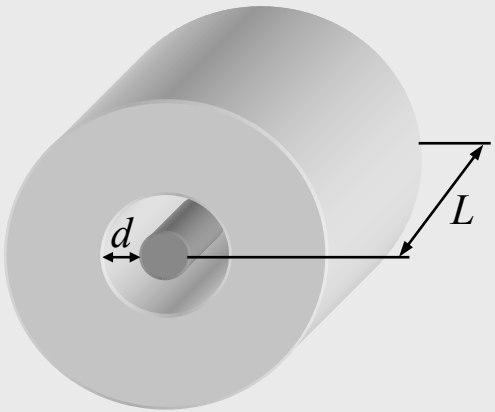
$\gamma(0)$ = 37 kJmol^{-1}nm^{-2}

Nanotube-Polymer Interaction Energies (ΔE_{np})



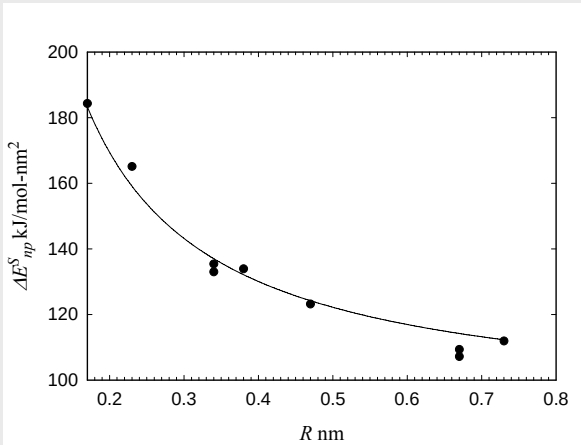
Models of CNT-Polystyrene Agglomerates Obtained using MM+ Force Field

Chiral Indices	Nanotube Radius (nm)	Nanotube Length (nm)	Number of 16-monomer Polystyrene Chains in the Agglomerate	ΔE^{S}_{np} (kJ mol^{-1}nm^{-2})
3_2	0.17	3.80	20	184.3
6_0	0.23	3.78	20	165.1
5_5	0.34	3.39	20	133.0
6_4	0.34	3.90	24	135.4
10_0	0.38	3.78	24	133.9
7_7	0.47	3.88	24	123.2
10_10	0.67	3.39	24	109.3
12_8	0.67	3.90	34	107.2
20_0	0.73	3.78	34	111.9



$$\Delta E^{S}_{np}(R) = \frac{\Delta E^{S}_{gp}}{2}\frac{2\pi\ell\left[R+(R+d)\right]}{2\pi\ell R} = \Delta E^{S}_{gp}\left(1+\frac{d}{2R}\right)$$

$$\Delta E^{S}_{gp} = 90.7 kJmol^{-1}nm^{-2}, d = 0.35nm$$

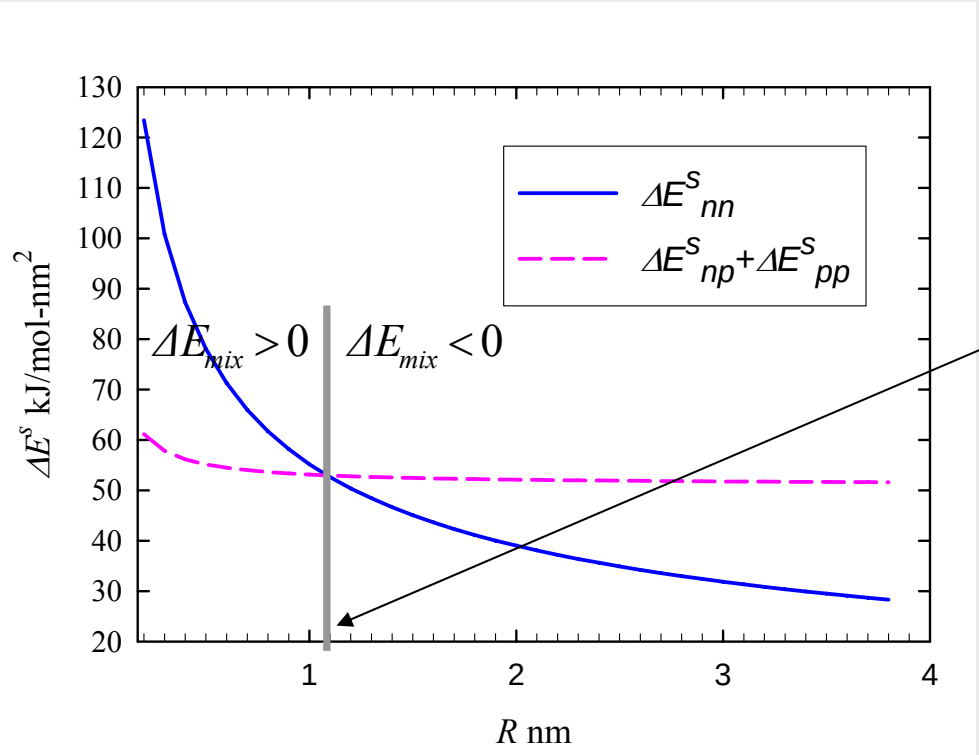


Dependence of Energy of Mixing on CNT Radius

$$E^{S}_{mix}(R) = \Delta E^{S}_{nn}(R) - \left[\Delta E^{S}_{np}(R) + \Delta E^{S}_{pp}(R)\right] = \frac{C_{nn}}{\sqrt{R}} - \left[(E^{S}_{gp} - \gamma_{pp}) + (\frac{E^{S}_{gp}}{2} - \gamma_{pp})\frac{d}{R}\right]$$

CNT bundle exfoliation

CNT extraction from polymer



$$R \approx \left[\frac{C_{nn}}{(\Delta E^{S}_{gp} - \gamma_{pp})}\right]^2$$

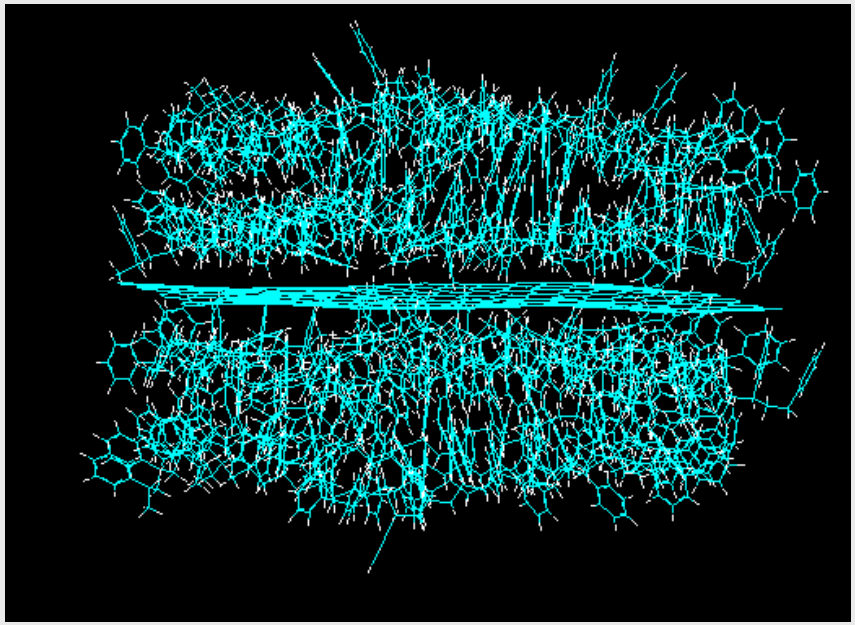
Energy of Mixing Multi-Walled CNTs

Since SWCNTs are typically smaller (R < 0.7 nm), the energy of mixing them with PS should be endothermic. For DWCNTs

$$R \approx \left[\frac{65.5\, kJmol^{-1} nm^{-3/2}}{(102.3 kJmol^{-1} nm^{-2} - 39.6 kJmol^{-1} nm^{-2})} \right]^2 = 1.09\ nm$$

which is about the same value we obtained for SWCNTs. Calculations indicate that the effect of additional walls is negligible. Thus, based on this analysis, we think that the energy of mixing MWCNTs (in PS) is always exothermic.

Dependence of Energy of Mixing on Shape



$$\frac{\Delta E_{mix}}{S_g} = \frac{\Delta E_{gg}}{S_g} - \left(\frac{2\Delta E_{gp}}{S_g} - \frac{2\Delta E_{gp}}{S_g} \right)$$

$$= 164\, kJmol^{-1}nm^{-2} - 2\left(90.7\, kJmol^{-1}nm^{-2} - 39.6\, kJmol^{-1}nm^{-2}\right)$$

$$= +62\ kJ/mol - nm^2$$

Mesoscale Model of Polymer-CNT Composite

The unique properties of polymer nanocomposites arise from interactions between nanoadditives and polymers that are limited to a range of about 10 nanometers. This is too small to be captured by continuum mechanics, but beyond the capabilities of conventional atom based molecular mechanics (MM) and dynamics. Problems that fall into this domain (commonly referred to as the mesoscale) can be handled by coarse-grained particle methods, such as dissipative particle dynamics (DPD), which require force fields that are resolved over meso, as opposed to atomic, length scales.

DPD

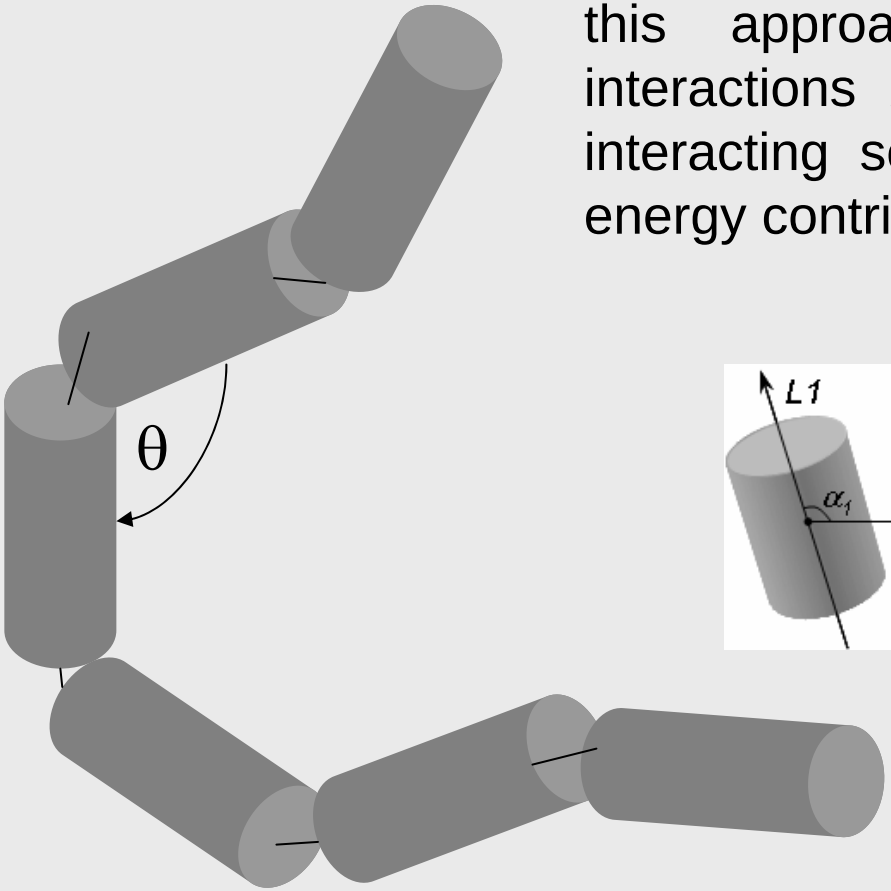
$$\dot{\mathbf{p}}_i = \mathbf{F}_i,$$

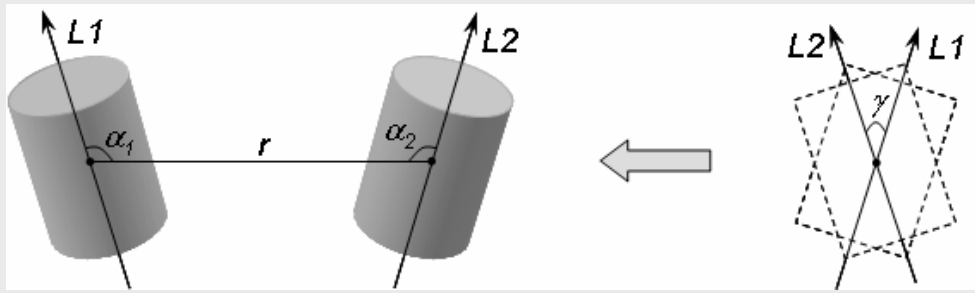
$$\mathbf{F}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R).$$

$$\mathbf{F}_{ij}^D = -\gamma w^D(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}$$

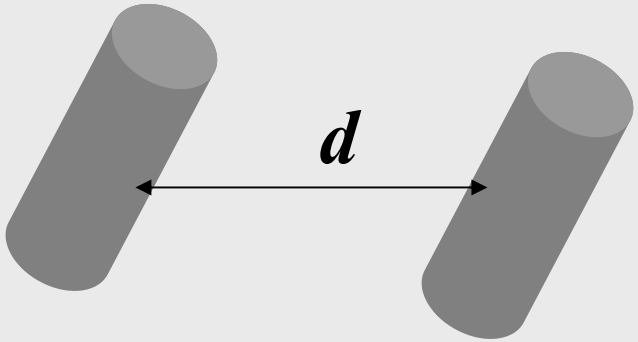
Course-Grained Representation of CNTs (F_{ij}^{C})

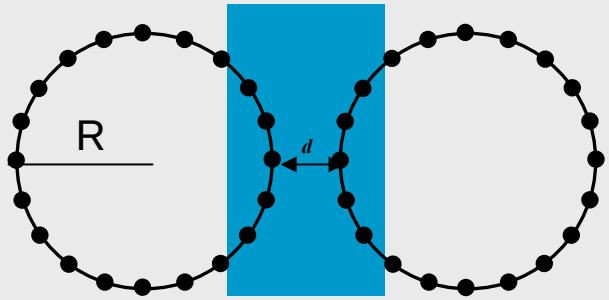
CNTs will be represented as a series of cylindrical segments connected by flexible joints that allow the angles between segments to vary. By employing this approach, the thousands of individual interactions between atoms contained within two interacting segments are integrated into a single energy contribution.





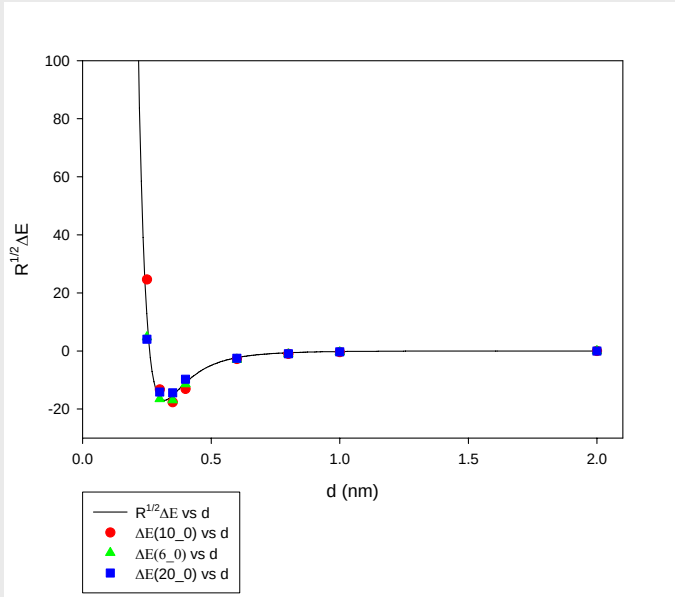
Interaction between CNTs





$$\Delta E(d) = \int v(d + \frac{x^2}{R}) dx = R^{1/2} \int v(d + \eta) d\eta$$

$$\frac{\Delta E(d)}{S_g} = \frac{\int v(d + \eta) d\eta}{2\pi R^{1/2} \ell}$$



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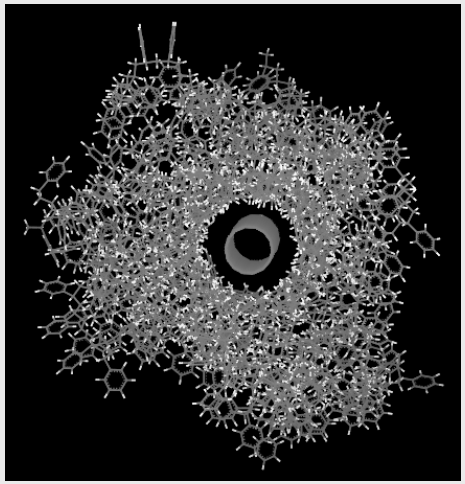
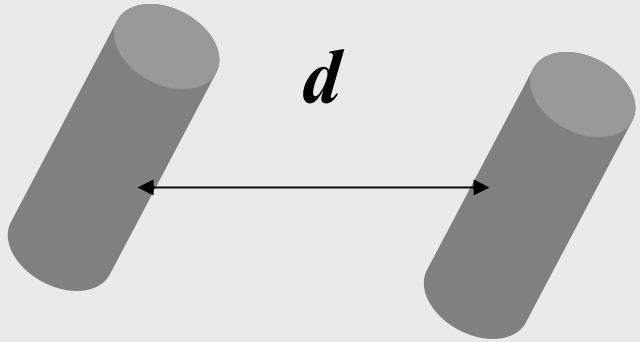
Interaction of CNTs with Polymer





$$\frac{dE}{dV}$$

$$\boldsymbol{F_{dep} = -\frac{\partial V}{\partial d}\frac{dE}{dV}}$$

Acknowledgements

Sam Manzello (BFRL/NIST), Takashi Kashiwagi (BFRL/NIST), Sameer Rahatekar (BFRL/NIST), Richard Lyon (FAA)