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Effective Dispersion of Boron Nitride Nanotubes for Composite Fabrication

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Motivation

- Boron nitride nanotubes (BNNTs) are a structural analog of CNTs composed of a hexagonal B-N bonding network.
- Excellent candidates for nanocomposites due to:
  - comparable mechanical properties to CNTs
  - excellent chemical and thermal stability
  - high thermal conductivity
  - piezoelectricity
  - radiation shielding capability
- Uniform dispersion is critical for harnessing the advantageous properties of the nanofiller in a nanocomposite.
- Need to overcome the intermolecular forces between individual nanotubes to prevent aggregation and bundling.

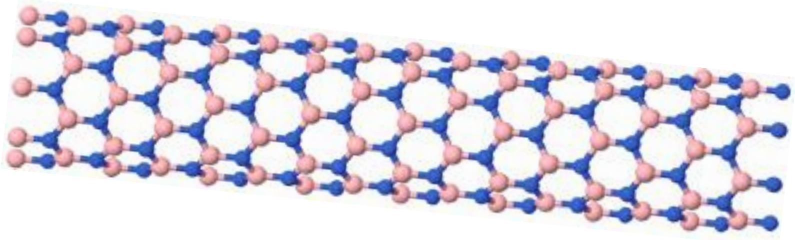

Image from Lin et al. *J. Phys.: Condens. Matter* **25** (2013) 295501.

Current techniques for improving nanotube dispersion:

1. Surface functionalization
2. Surfactants
3. High-power sonication
4. Polymer wrapping

These methods modify or damage the raw nanotube surface and/or structure which is often detrimental to their properties in a nanocomposite.

Background: Solution Thermodynamics and Solubility Theory

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- Solution thermodynamics describes the mixing of multiple components (i.e. solvents and BNNTs) by the Gibbs free energy (ΔG_{mix}) of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

ΔH_{mix}= enthalpy of mixing
T= temperature in Kelvin
ΔS_{mix}= entropy of mixing

- If ΔG_{mix} is negative, the components will spontaneously mix to form a homogeneous solution → Need to minimize ΔH_{mix}[1]→ Hansen solubility theory!
- Based on the idea that "like dissolves like" in order to minimize ΔH_{mix}.
  - Match the Hansen solubility parameters (δ_d, δ_p, δ_h) of the solvent to the solute.

δ_d= dispersion component (non-polar)
δ_p= polar component (permanent dipole-dipole interactions)
δ_h= hydrogen bonding component

- The Hansen solubility parameters represent the Hildebrand parameter (δ_t):[2]

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

1. Bergin et al. *Adv. Mater.* **20** (2008) 1876 - 1881 and Hughes et al. *Nanotech.* **23** (2012) 265604.
2. C.M. Hansen "Hansen Solubility Parameters: A User's Handbook" Taylor & Francis, 2007.

The Approach

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- By correlating the dispersion state of BNNTs in single solvents with the known Hansen solubility parameters a 3D Hansen space plot (Figure 1) can be generated to determine the solubility region of BNNTs.
- Solvent blends are mixtures of two or more solvents which can enhance dispersion stability.
  - Does not alter nanotube surface, can enhance the solubility of individual solvents, economical, and environmentally-friendly.
- Suitable solvent blends can be chosen from the solubility region.
  - The solubility parameters can be tailored by varying the ratio of the two solvents, by creating a tie-line between the two (Figure 2).

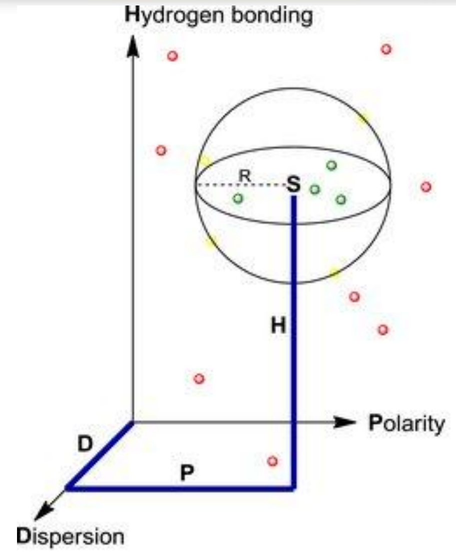

Figure 1: An example of 3D Hansen space.[1]

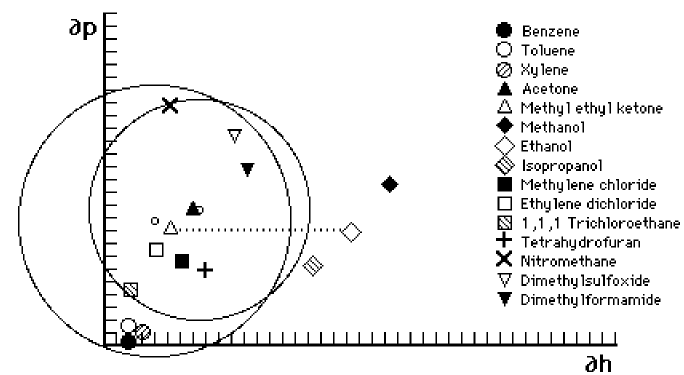

Figure 2: Choosing solvent blends for a solute.[2]

1. http://confidentsolventselection.com/about/solubility-parameters.html
2. http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html

Experimental Procedure

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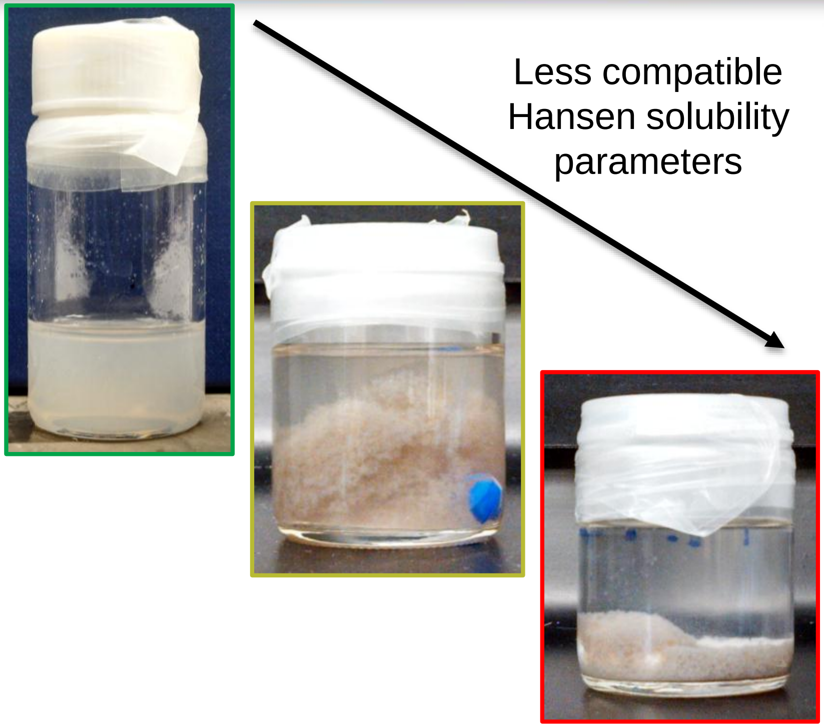
- 5 mg of BNNTs were mixed with 20 mL of solvent(s)
- Samples were stirred continuously 4 days, then sonicated for two 15 minute segments.
  - Samples were monitored at 24 hours, 1 week, 1 month, and 2 months.
- In addition to visual inspection, some samples were characterized with scanning electron microscopy (SEM) and UV-Visible spectroscopy (UV-Vis).



The dispersion state is characterized in one of three ways:[1]

1. Dispersed: maintains a uniform color without aggregation or precipitation
2. Swollen: aggregated nanotubes and phase separation are observed
3. Sedimented: large aggregations; material rapidly precipitates after agitation

1. Ham et al. *J. Colloid. Int. Sci.* **286** (2005) 216 – 223.

Single solvent studies

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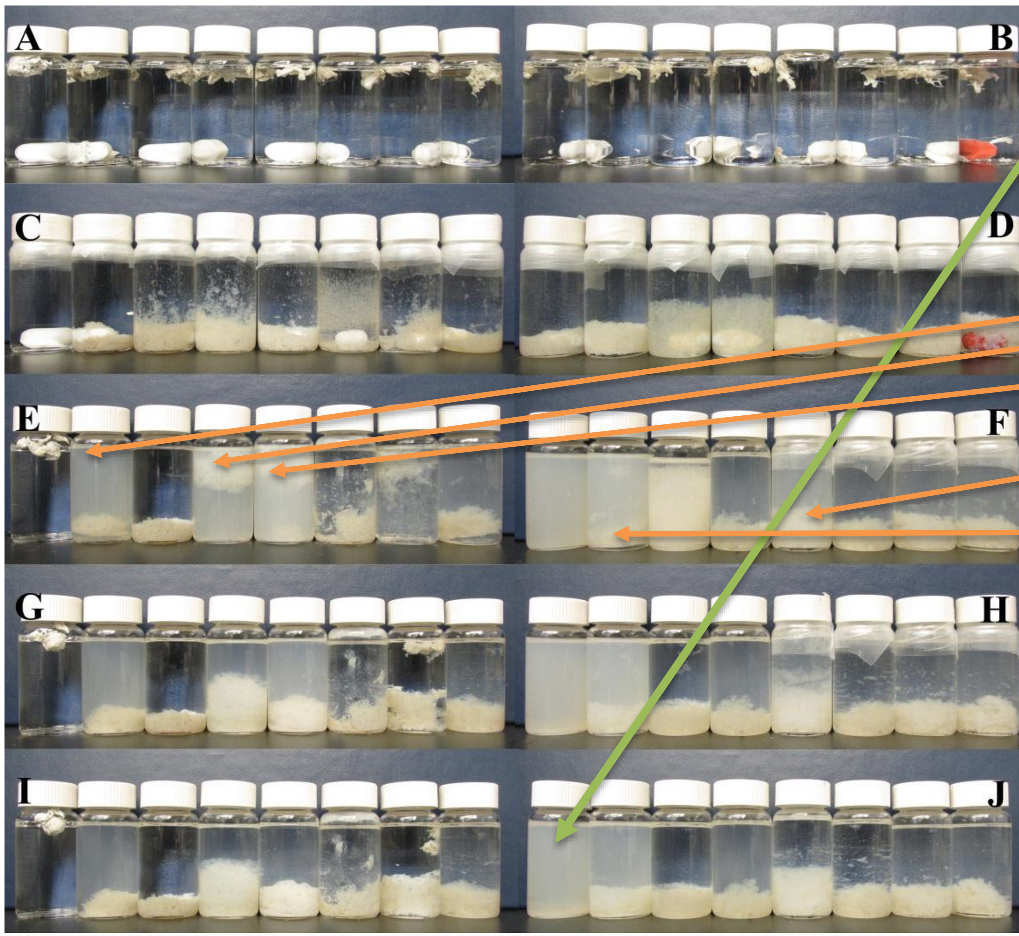
Solvents from left to right:

water, acetone, ethanol (EtOH), isopropanol (IPA), methanol (MeOH), hexane, acetic acid, and toluene

Dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP), tetrahydrofuran (THF), pyridine, chloroform, and dichloromethane (DCM)

Before stirring → After stirring for 4 days → After 30 mins of sonication → 24 hours of settling time → 1 week of settling time



DMAc displayed a uniform, stable dispersion after 1 week.

DMF, THF, MeOH, IPA, and acetone showed substantial short-term dispersion.

The remaining solvents displayed fast sedimentation of BNNTs even after sonication.

Single solvent studies, continued

Solvent	δ_d $MPa^{1/2}$	δ_p $MPa^{1/2}$	δ_h $MPa^{1/2}$	δ_t $MPa^{1/2}$	Structure	Dispersion state (stirring only)	Dispersion state (stirring + 30 mins sonication)
N,N'-dimethylacetamide (DMAc)	16.8	11.5	10.2	22.5	$CH_3C(O)N(CH_3)_2$	sedimented	dispersed
N,N'-dimethylformamide (DMF)	17.4	13.7	11.3	24.9	$HC(O)N(CH_3)_2$	swollen	dispersed/swollen
tetrahydrofuran (THF)	16.8	5.7	8.0	19.4	$(CH_2)_4O$, cyclo	swollen	dispersed/swollen
methanol	15.1	12.3	22.3	29.6	CH_3OH	swollen	dispersed/swollen‡
isopropyl alcohol (IPA)	15.8	6.1	16.4	23.6	$(CH_3)_2CHOH$	swollen	dispersed/swollen‡
acetone	15.5	10.4	7.0	19.9	CH_3COCH_3	sedimented	dispersed/swollen
N-methyl-2-pyrrolidone (NMP)	18.0	12.3	7.2	23.0	$HN((CH_2)_3CO)$, cyclo	swollen	swollen†
chloroform	17.8	3.1	5.7	19.0	$CHCl_3$	sedimented	swollen†
dichloromethane	18.2	6.3	6.1	20.0	CH_2Cl_2	swollen	swollen†
acetic acid	14.5	8.0	13.5	21.4	CH_3COOH	swollen*	swollen†,‡
dimethylsulfoxide (DMSO)	18.4	16.4	10.2	26.7	$(CH_3)_2SO$	swollen	swollen
toluene	18.0	1.4	2.0	18.2	$C_6H_5CH_3$	sedimented	swollen†
pyridine	19.0	8.8	5.9	21.8	C_5H_5N, cyclo	sedimented	sedimented†
ethanol	15.8	8.8	19.4	26.5	C_2H_5OH	swollen	sedimented
hexane	15.3	0.0	0.0	15.3	$CH_3(CH_2)_4CH_3$	sedimented#	sedimented
water	15.6	16.0	42.3	47.8	H_2O	n/a*	n/a*

*Some raw BNNT pieces remaining on top of vial. In water, all raw BNNTs were unaffected by the processing methods; pieces remained on top of the solution.

†Minor milkiness was observed indicating a small amount of BNNTs were dispersed.

‡Swollen BNNT were suspended at the top of the solution immediately following sonication.

#BNNTs were broken up but adhered to the walls of the sample vial.

SEM analysis

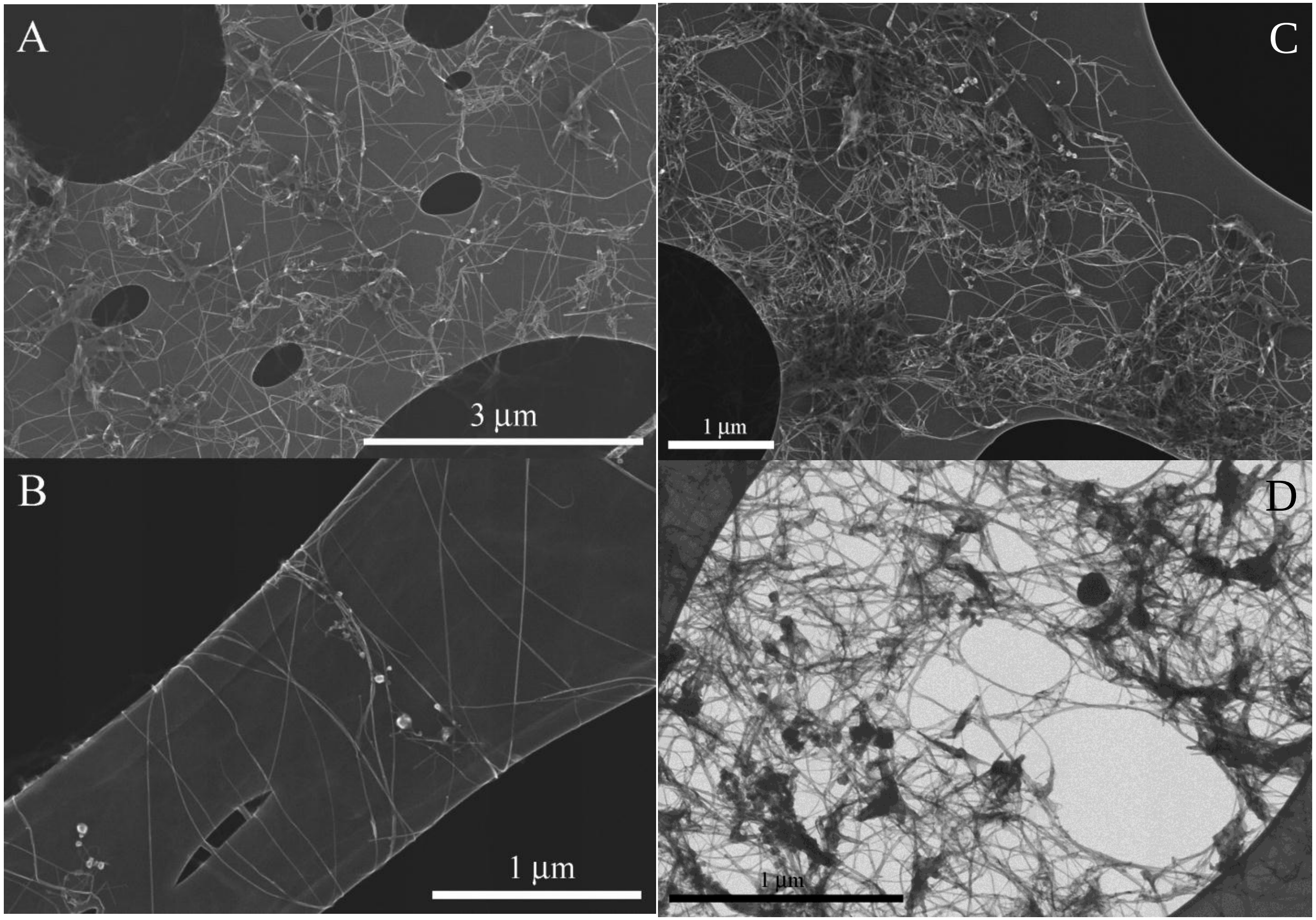
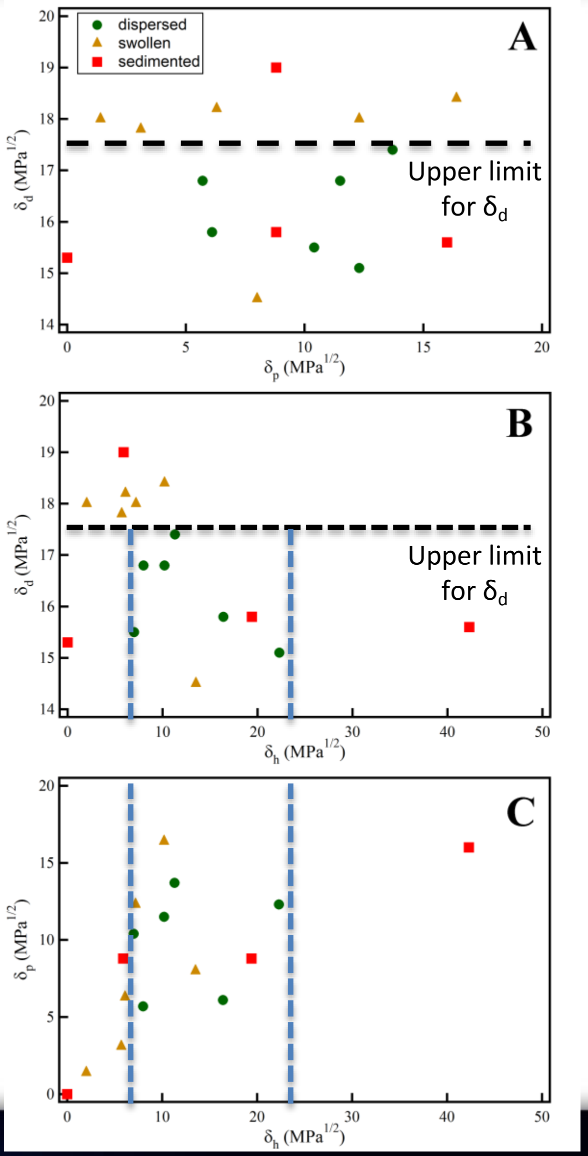


Figure 1. BNNTs from DMAc dispersion after 30 minutes of sonication (A, B) and as-synthesized BNNTs (C, D).

- No significant differences observed between raw tubes and BNNTs sonicated in DMAc.
- 30 minutes of sonication is sufficient to disperse BNNTs without any apparent damage from SEM imaging.
- Length/diameter aspect ratio of 364.
- High-resolution TEM imaging needed to confirm the nanotube structure is intact.

Single solvent studies, continued

- To determine a region of BNNT solubility, the Hansen solubility parameters were plotted as a function of the dispersion state.
- Based on these 2D plots, some observations can be made:
  1. The dispersion component appears to have an upper limit of 17.4 $MPa^{1/2}$ (A,B).
  2. Best dispersions exists for solvents within a moderate hydrogen bonding range (B,C).
- The solubility region of BNNTs is within a range of 15.5 – 17.4, 5.7 – 13.7, and 7.0 – 22.3 $MPa^{1/2}$ for δ_d, δ_p, and δ_h, respectively.
- Our results reinforce that the individual Hansen solubility parameters can more accurately describe the interaction between BNNTs and solvents over δ_t.[1]
  - For example, the value of δ_t for DMAc and pyridine are 22.5 and 21.8, respectively. DMAc is an excellent solvent while pyridine is a poor solvent.



1. Ham et al. *J. Colloid. Int. Sci.* **286** (2005) 216 – 223.

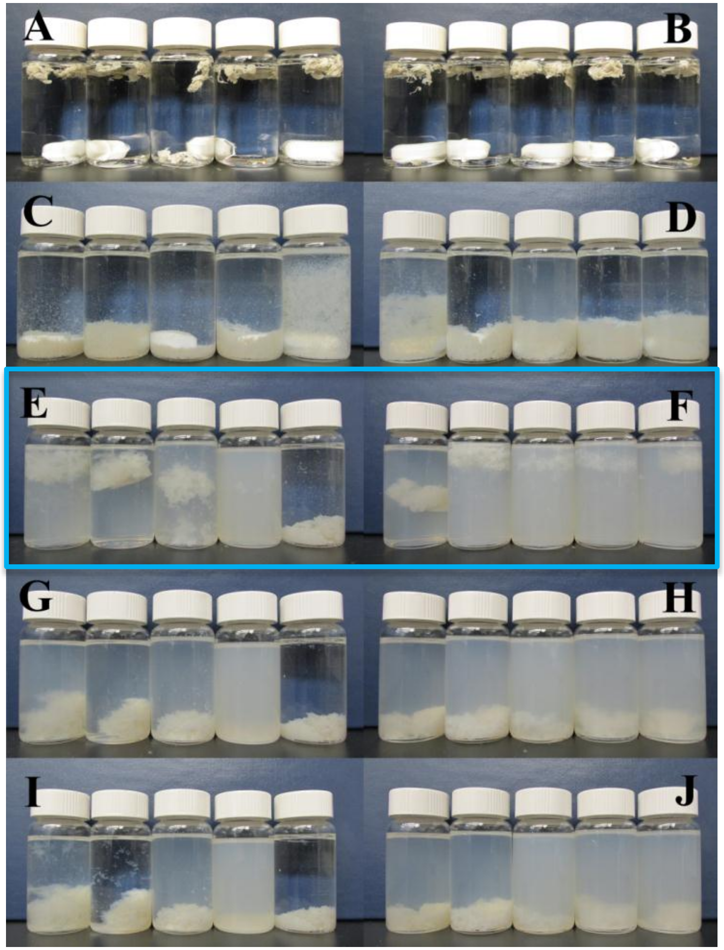
Solvent blend studies

Solvent blends from left to right:

IPA-DMF, DMF-DCM, hexane-THF, DMF-toluene, and DMAc-water

NMP-DMAc, EtOH-acetone, DMF-acetone, THF-NMP, and DMSO-THF

Before stirring → After stirring for 4 days → After 30 mins of sonication → 24 hours of settling time → 1 week of settling time



- Solvent blends were tailored to lie within the solubility region.
- 8 out of the 10 systems chosen contain poor stand-alone solvents.

Almost all solvent combinations maintain dispersed BNNTs after sonication in conjunction with swollen BNNTs.

Solvent blend studies

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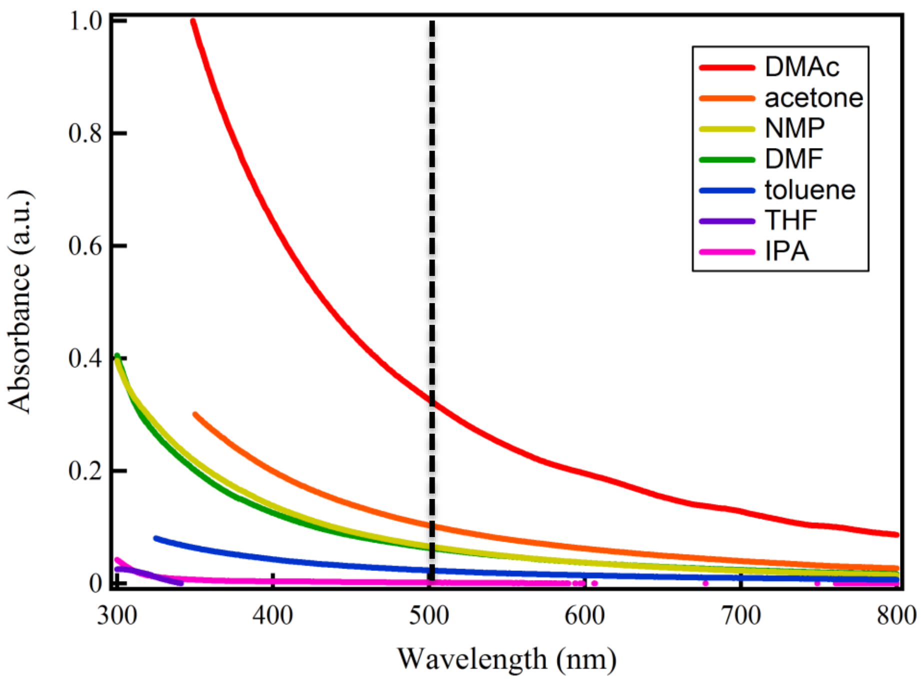
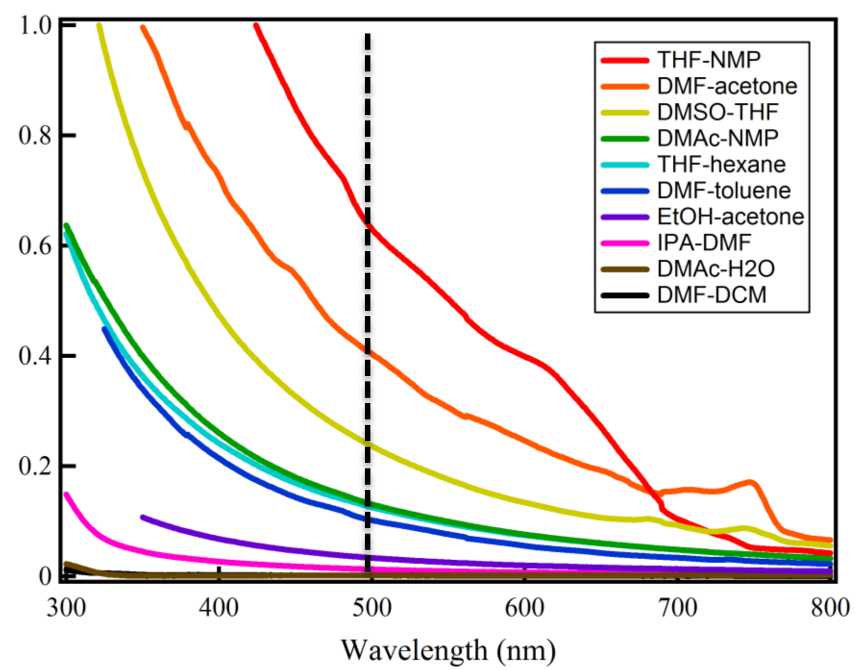
Solvent blend (50:50 ratio)	δ_d, $MPa^{1/2}$	δ_p, $MPa^{1/2}$	δ_h, $MPa^{1/2}$	δ_t, $MPa^{1/2}$	Dispersion state (stirring only)	Dispersion state (stirring + 30 mins sonication)
THF-NMP	17.4	9.0	7.6	21.0	swollen	dispersed/swollen‡
DMF-acetone	16.5	12.1	9.2	22.4	swollen†	dispersed/swollen‡
NMP-DMAc	17.4	11.9	8.7	22.8	swollen†	dispersed/swollen
DMSO-THF	17.6	11.1	9.1	23.1	swollen	dispersed/swollen‡
DMF-toluene	17.7	7.6	6.7	21.6	swollen	dispersed
IPA-DMF	16.6	9.9	13.9	24.3	sedimented	dispersed/swollen‡
ethanol-acetone	15.7	9.6	13.2	23.2	swollen	dispersed/swollen‡
DMF-DCM	17.8	10.0	8.7	22.5	swollen	dispersed/swollen‡
hexane-THF	16.1	2.9	4.0	17.4	sedimented	dispersed/swollen
DMAc-water	16.2	13.8	26.3	35.2	swollen	sedimented

†Minor milkiness was observed indicating a small amount of BNNTs were dispersed.
‡Swollen BNNT were suspended at the top of the solution immediately following sonication.

- Stable dispersions of BNNTs can be generated although several solvent blends contain poor stand-alone solvents (i.e. toluene, hexane, ethanol, etc.) by tailoring the solubility parameters to match BNNT.
  - Stability was significantly enhanced as compared with many individual solvent.
- All solvent blends, except DMAc-water, displayed dispersed BNNTs after 30 minutes of sonication.
  - The poor solubility of the DMAc-water system is likely due to the large hydrogen bonding component of 26.3 $MPa^{1/2}$.

Long term stability - UV-Vis data





- Selected single solvents (left) and all solvent blends (right) were analyzed after 2 months of settling time.
- At an arbitrary point of 500 nm, the absorbances of all samples were compared. The UV-Vis data reinforced our conclusions from visual observations over time.
- We found that two solvent blends (THF-NMP and DMF-acetone) displayed higher absorbance values than DMAc alone, which demonstrates the effectiveness of solvent blends and our approach to BNNT solubility.

Applying to nanocomposites

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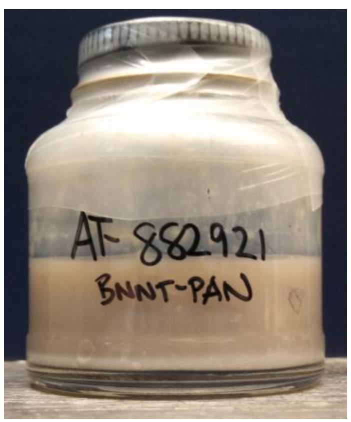
- By treating polymers as co-solvent in a solvent blend, we selected suitable solvent-polymer combinations to effectively disperse BNNTs.
- The well-dispersed BNNTs were subsequently utilized for the fabrication of nanocomposite and mats up to 75 wt% BNNT.

Example of polymer solvent blends

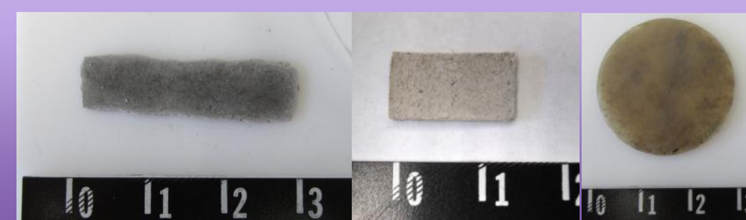


Polyacrylonitrile

Polyurethane

Composite & mat fabrication

BNNT Composites (up to 75 wt%)



BNNT Mats (up to 50 wt%)

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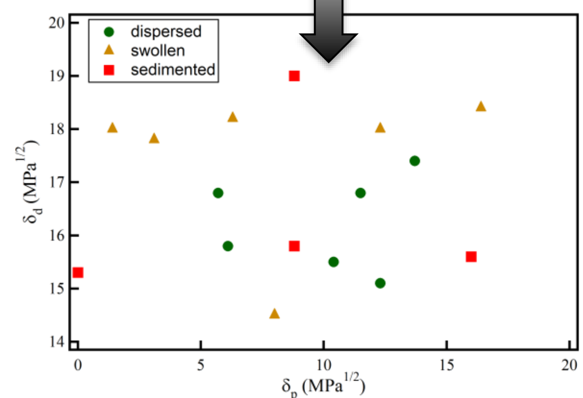
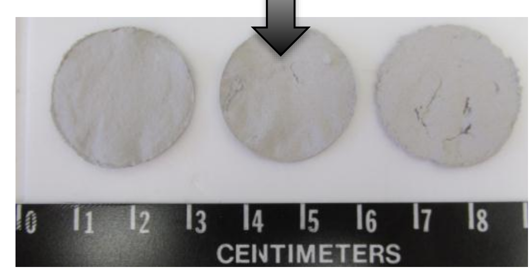
Summary

- Applied Hansen solubility theory to dispersing BNNTs.
- By correlating the known solubility parameters to the dispersion state of BNNTs in single solvents, we were able to determine a region of good solubility for BNNTs.
  - DMAc was found to be the best single solvent.
- Applying this knowledge, we chose suitable solvent blends for BNNTs by tailoring the solubility parameters.
- Several solvent blends maintained a higher concentration of BNNTs than single solvents alone, reinforcing the effectiveness of this approach.
  - THF-NMP and DMF-acetone were the best solvent blends.
- We extended this to the fabrication of nanocomposites and mats of BNNTs by creating solvent blends with polymers. Able to generate nanocomposites up to 75 wt% BNNT.





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