Supporting Information for

Boron Nitride Nanotubes: Force Field Parameterization, Epoxy Interactions, and Comparison with Carbon Nanotubes for High Performance Composite Materials

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S1. IFF-R parameters for B and N in h-BN

Table S1 and Table S2 shows the IFF-R parameters developed for B and N atoms for h- BN.

Table S1: Masses of atoms

Atom (atom type in the forcefield)	**Mass** (grams/mol)
Boron (bbn)	8.81100
Nitrogen (nbn)	12.00670
Virtual electron (bbe or nbe)	1.000000

Table S2: IFF parameters for boron, nitrogen, and virtual electrons in h-BN using the PCFF energy expression.

Bonds (harmonic)*	r_{ij}	$K_{bond,ij}$ (kcal/mol)
nbn-nbe, bbn-bbe	0.65 Å	250
bbn-nbn	1.485 Å	75
Angles (harmonic)**	θ_{ij}	$K_{angle,ij}$ (kcal/mol)

nbe-nbn-nbe, or bbe-bbn-bbe	180°	50
nbe-nbn-bbn, bbe-bbn-nbn	90°	50
nbn-bbn-nbn, bbn-nbn-bbn	120°	90
Charge	***q*** (coulomb)	
Nitrogen (nbn)	-0.25 e	
Boron (bbn)	+0.65 e	
Virtual electron (nbe or bbe)	-0.10 e	
9-6 LJ sigma	$\sigma_{0,ii}$ (Å)	
nbn or bbn	4.34	
nbe or bbe	0.0	
9-6 LJ epsilon	$\varepsilon_{0,ii}$ (kcal/mol)	
nbn or bbn	0.062	
nbe or bbe	0.0	

[a] *Only the harmonic bond constant (k_{bond2}) is used, k_{bond3} and k_{bond4} are not needed and set to 0 in the PCFF bond equation.

$$E_{bond} = k_{bond\,2}(r-r_0)^2 + k_{bond\,3}(r-r_0)^3 + k_{bond\,4}(r-r_0)^4 \tag{1}$$

[b] **Only the harmonic angle constant (k_{angle2}) is used, k_{angle3} and k_{angle4} are not needed and set to 0 in the PCFF angle equation

$$E_{angle} = k_{angle2}(\theta-\theta_0)^2 + k_{angle3}(\theta-\theta_0)^3 + k_{angle4}(\theta-\theta_0)^4 \tag{2}$$

[c] The angle bending constants for BNNT may be somewhat approximate and more specific training has not been carried out since the parameters yield a good match with experimental vibration spectra. Computed interfacial properties are hardly affected (few percent), however, even if the angle bending constants would be varied up to ±30%. The force field is thus expected to perform nearly identical with or without further iteration of the angle bending constants, and it may be challenging to validate the effects.

[d] The LJ parameters for B and N in BN are difficult to distinguish from C atoms in graphene because the structures of BN and graphene are isoelectronic. The LJ parameters for B and for N were thus chosen identical to graphene here. The major difference lies in the charge distribution, which is quantitatively represented by the dedicated atomic charges of B and N. The effect of modifications of the LJ parameters for B and N in a reasonable range is expected to be minor, estimated to change surface and binding energies by less than 10%.

S2. Mass Ratio Calculations

Table S3: Mass ratio for EPIKURE W:EPON 862

Resin	EPON 862	Hardener	EPIKURE W (DETDA)
Formula	$C_{19}H_{20}O_4$	Formula	$C_{11}H_{18}N_2$
Molecular weight (g/mol)	312.4	Molecular weight	178

The MD simulations employed a 2:1 stoichiometric ratio for EPON 862:EPIKURE W.

2:1 stoichiometric ratio → weight ratio of (2*312.4):(1*178.3) = **100:28.5**. Note this ratio is slightly higher than the manufacturer recommended mixing ratio of 26.4 parts hardener per hundred parts resin by weight.

Table S4: Mass ratio for EPIKURE 3223:EPON 828

Resin	EPON 828	Hardener	EPIKURE 3223 (DETA)
Formula	$C_{21}H_{24}O_4$	Formula	$C_4H_{13}N_3$
Molecular weight (g/mol)	340.4	Molecular weight	103.2

MD simulation employed a 5:2 stoichiometric ratio for EPON 828:EPIKURE 3223.

5:2 stoichiometric → weight mass ratio of (5*340.4):(2*103.2):(5*340.41) = 12.1:100:12.1. Note this ratio is approximately equal to the manufacturer recommended mixing ratio of 12 parts hardener per hundred parts resin by weight.

S3. Molecular Modeling

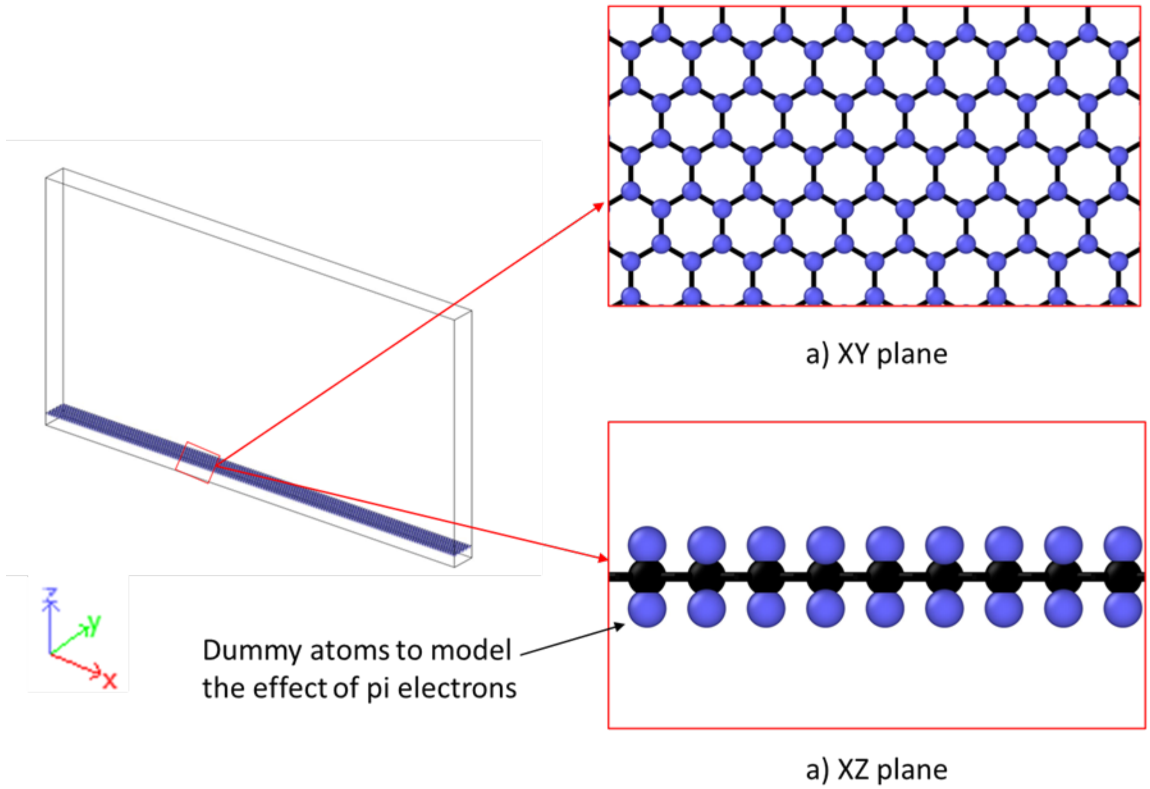

Figure S1 : Molecular model of CNT surface with a) CNT surface view in the XY plane and b) CNT surface view in the XZ plane with dummy atoms to model the effect of pi electrons

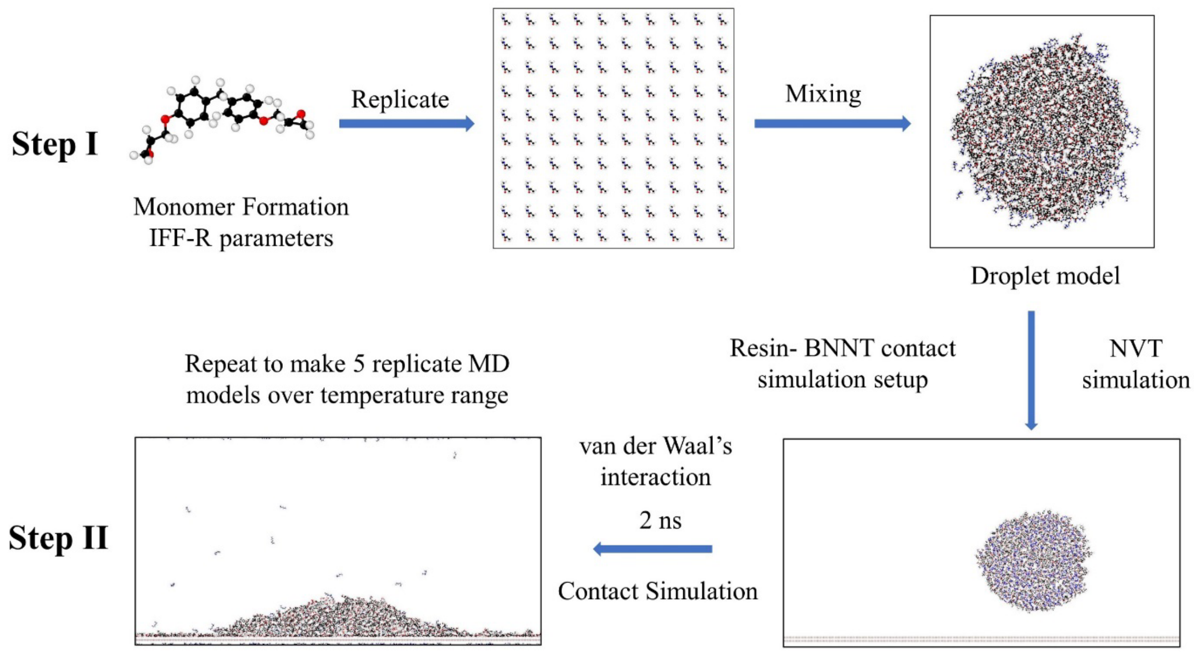

Figure S2: MD simulation procedure. Step I: Droplet formation, Step II: Contact simulations

Table S5: Number of atoms in the droplet models per resin system

Resin	Number of atoms in droplet model
Bisphenol-F epoxy with aromatic hardener	15,444
Bisphenol-A epoxy with aliphatic hardener	15,960
Bisphenol-F epoxy with aliphatic hardener	15,300
Bisphenol-A epoxy with aromatic hardener	15,480

S4. Simple infusion and curing

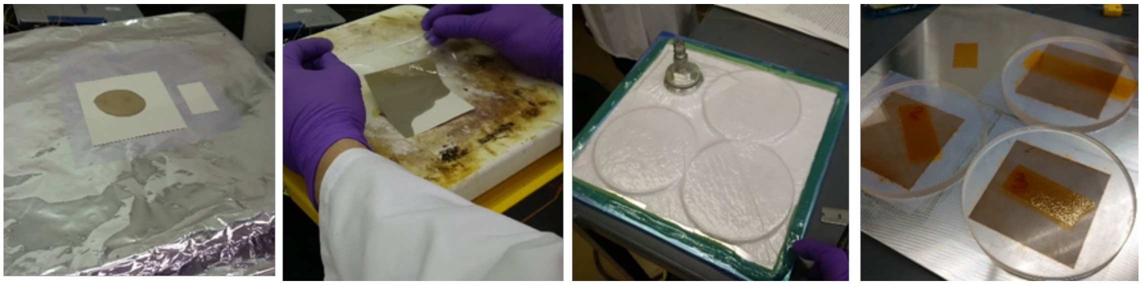

Figure S3: Simple infusion and vacuum bag curing of BNNT buckypaper-epoxy composites

Table S6: Comparison of CNT and BNNT epoxy composites in simple epoxy infusion test of CNT and BNNT buckypaper samples. Thicknesses were measured using a micrometer and nanotube wt.% was determined from the masses of the initial buckypaper and final composites.

Nanotube type	Buckypaper density (g cm^{-3})	Buckypaper-epoxy composites		Thickness change (%)
		Nanotube wt%	Density (g cm^{-3})	
CNT	0.33	21%	1.25	+23%
BNNT	0.39	32%	1.37	-8%

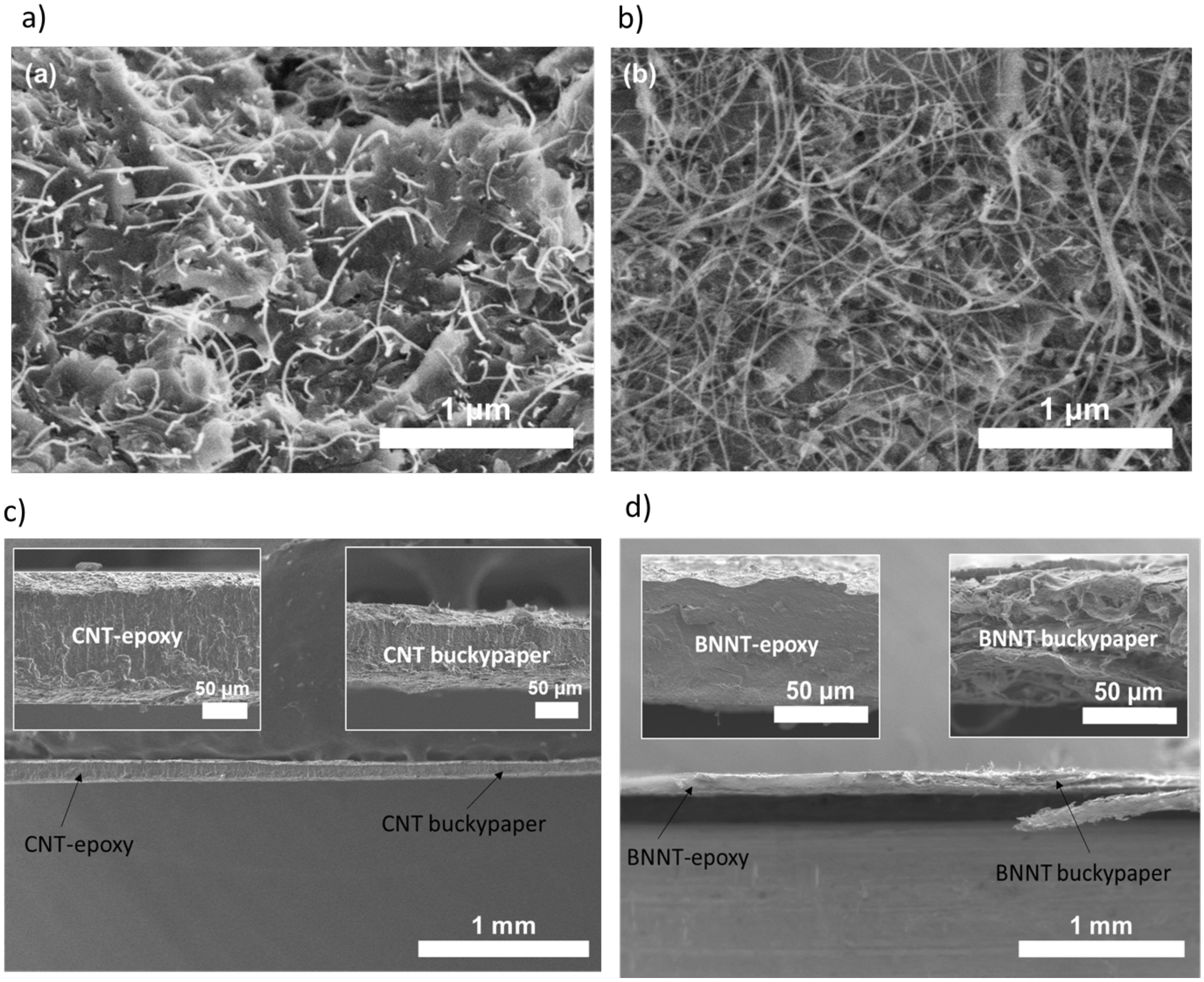

Figure S4: SEM images of cross-section, fracture surfaces of a) CNT-buckypaper-epoxy and b) BNNT-buckypaper-epoxy composites c) Cross sections of partially infused CNT buckypaper d) Cross sections of partially infused BNNT buckypaper, where only half of a buckypaper strip was wetted with epoxy. Thickness increased in the area of the epoxy infusion

S5. Experimental Contact Angle Values

Figure S5- S8 represents the contact angle values recorded in experiments as a function of time following placement of a drop of epoxy. The horizontal axis represents the total test time of 60 s, and mean contact angle values recorded are plotted on the vertical axis.

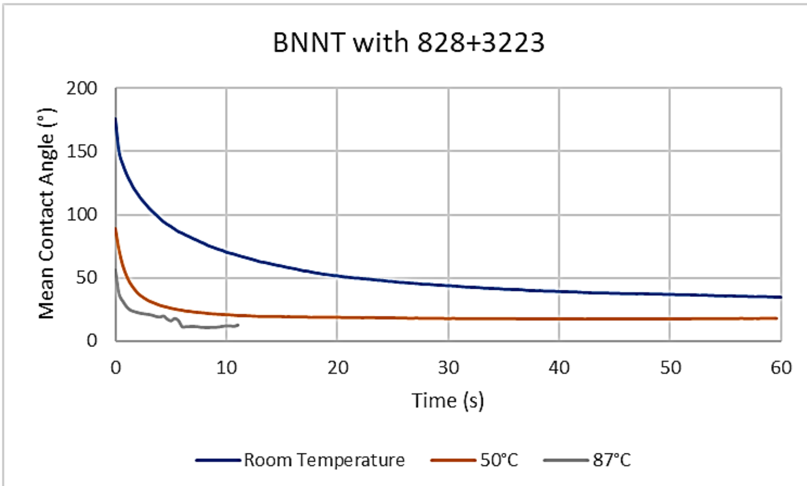

Figure S5: Mean contact angle with test time in experiments for the bisphenol-A epoxy system on the BNNT buckypaper surface at different temperatures.

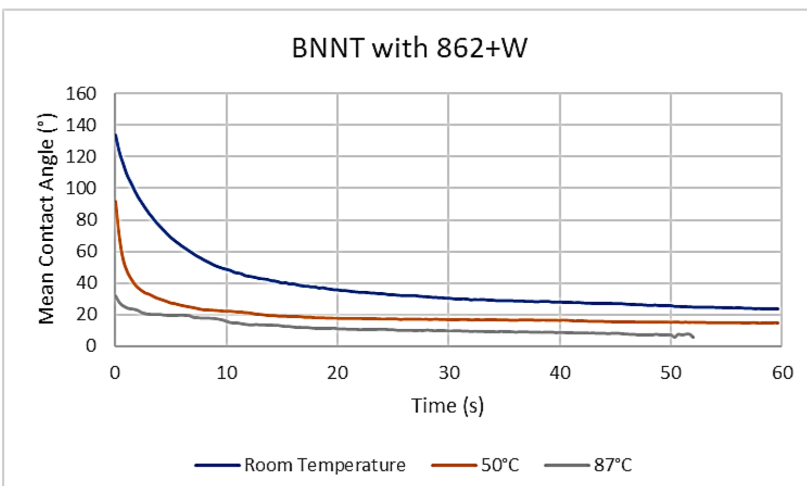

Figure S6: Mean contact angle with test time in experiments for the bisphenol-F epoxy system on the BNNT buckypaper surface at different temperatures.

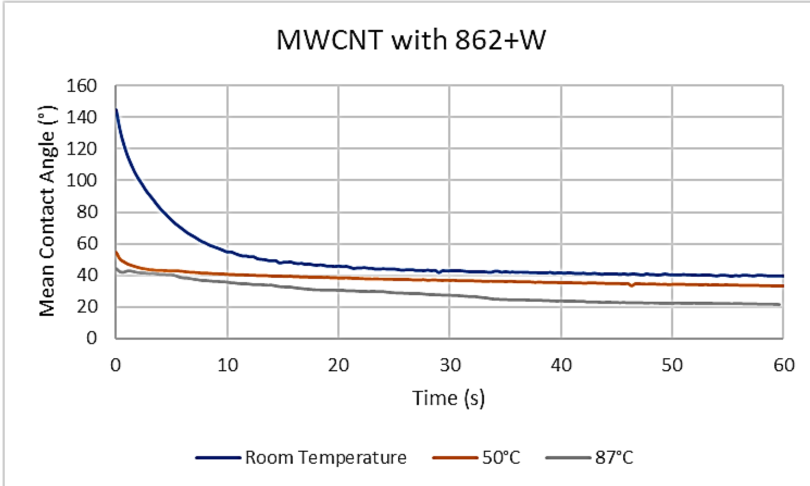

Figure S7: Mean contact angle with test time in experiments for the bisphenol-F epoxy system on the CNT buckypaper surface at different temperatures.

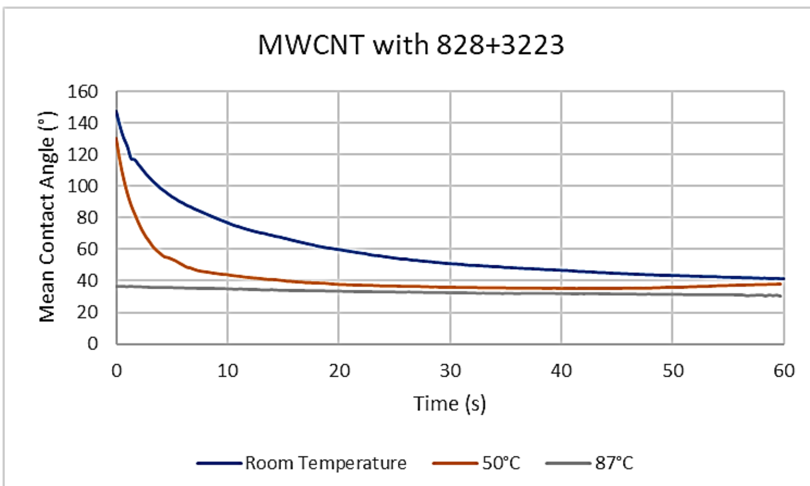

Figure S8: Mean contact angle with test time in experiments for the bisphenol-F epoxy system on the CNT buckypaper surface at different temperatures.

S6. Adsorption of phenyl rings on BNNT

Figure S9 shows the preferential adsorption of phenyl rings on BNNT surface in bisphenol-A based epoxy resin with aromatic hardener system. Figure S9 shows the last snapshot of the contact simulation at 147 °C as a representative image.

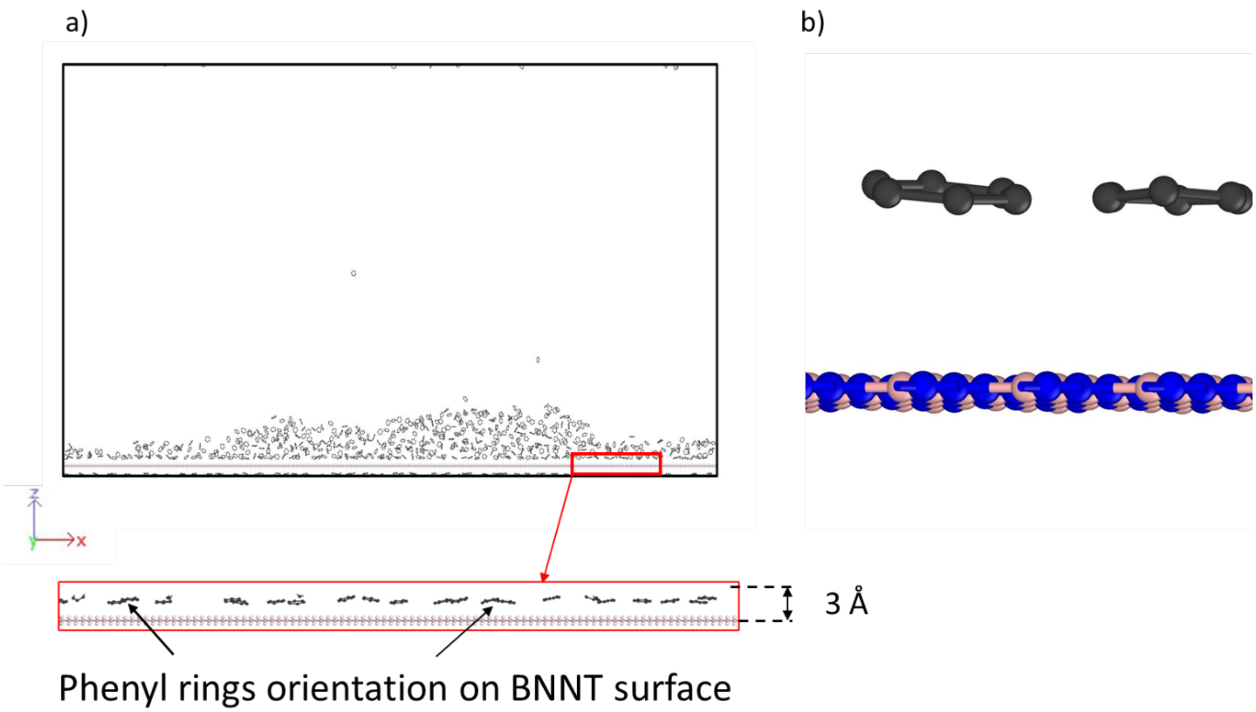

Figure S9: Adsorption of phenyl rings on BNNT surface for bisphenol-A epoxy with aromatic hardener a) Orientation of phenyl rings shown in XZ plane b) Enlarged view in XZ plane without virtual pi electrons

S7. Contact angle values

A. Experiments

Contact angle values calculated from the experiments are listed in Tables S7 – S9.

Table S7: Final contact angles as measured at room temperature

	Buckypaper type	Final Contact Angle (degrees)	Mean Contact Angle AVG ± STD (degrees)
Epon862+W	MWCNT	39.9	39.1 ± 0.6
		39.4	
		38.1	
		39.3	
	BNNT	23.9	24.3 ± 0.5
		25.0	
		24.0	
Epon828+3223	MWCNT	46.8	44.2 ± 2.4
		41.9	
		46.3	
		41.6	
	BNNT	34.8	35.5 ± 1.2
		34.4	
		37.2	

Table S8: Final contact angles as measured at ~50°C

		Final Contact Angle (degrees)	Mean Contact Angle AVG ± STD (degrees)
Epon862+W	MWCNT	44.3	40.2 ± 4.1
		40.2	
		33.5	
		42.6	
	BNNT	17.1	15.5 ± 1.1
		14.8	
		15.8	
Epon828+3223	MWCNT	42.3	40.8 ± 2.0
		42.1	
		37.9	
	BNNT	12.1	14.4 ± 2.4
		17.6	
		13.4	

Table S9: Final contact angles as measured at ~87°C

		Final Contact Angle (degrees)	Mean Contact Angle AVG ± STD (degrees)
Epon862+W	MWCNT	21.6	22.6 ± 1.8
		22.9	
		20.6	
		25.5	
	BNNT	10.1	8.6 ± 1.4
		7.4	
		7.0	
		9.7	
Epon828+3223	MWCNT	30.0	33.2 ± 3.8
		31.1	
		38.6	
	BNNT	8.4	10.6 ± 1.6
		12.3	
		11.0	

B. MD Simulations

Table S10: Contact angle values predicted by MD simulations on BNNT surface.

Temperature (°C)	Bisphenol-F epoxy resin		Bisphenol-A epoxy resin	
	Aromatic Hardener	Aliphatic Hardener	Aromatic Hardener	Aliphatic Hardener
87	41.6 ± 2.3	47.1 ± 2.9	29.4 ± 3.0	37.6 ± 3.5
117	30.9 ± 3.2	37.5 ± 3.2	29.2 ± 3.5	28.5 ± 2.9
147	20.8 ± 1.5	27.5 ± 2.5	17.9 ± 2.2	19.2 ± 3.0
177	12.7 ± 2.6	18.7 ± 1.8	19.2 ± 0.9	13.1 ± 0.4