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Self-Assembly of Carbon Nanotubes in Polymer Melts: Simulation of Structural and Electrical Behaviour by Hybrid Particle-Field Molecular Dynamics

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Supporting Information

Hybrid MD-SCF CG models

For both models, carbon nanotube (CNT) and polymers (homo and copolymer blocks) bonds between two successive beads are described by a harmonic potential:

$$V_{bond}(R) = \frac{1}{2} K_{bond} (R - R_{bond})^2 \qquad (1)$$

where the equilibrium distance R_{bond} =1.12 nm for the CNT and 1.4 nm for the homo and block copolymer. K_{bond} = 10000 kJ·mol^{-1} is the bond force constant (for both models). The stiffness of the CNT is taken into account by a harmonic potential depending on the cosine of angle between beads, where θ is the angle between two successive bonds. In the equation 2 is reported the functional form of angle potential:

$$V_{angle}(\theta) = \frac{1}{2} K_{angle} \{\cos(\theta) - \cos(\theta_0)\}^2 \qquad (2)$$

where θ_0 = 180° is the equilibrium bond angle for CNT, and K_{angle} = 8000 kJ·mol^{-1} is the angle force constant. Additionally, the CG model of CNT has the diameter D = 2.8 nm (Figure S1 a).

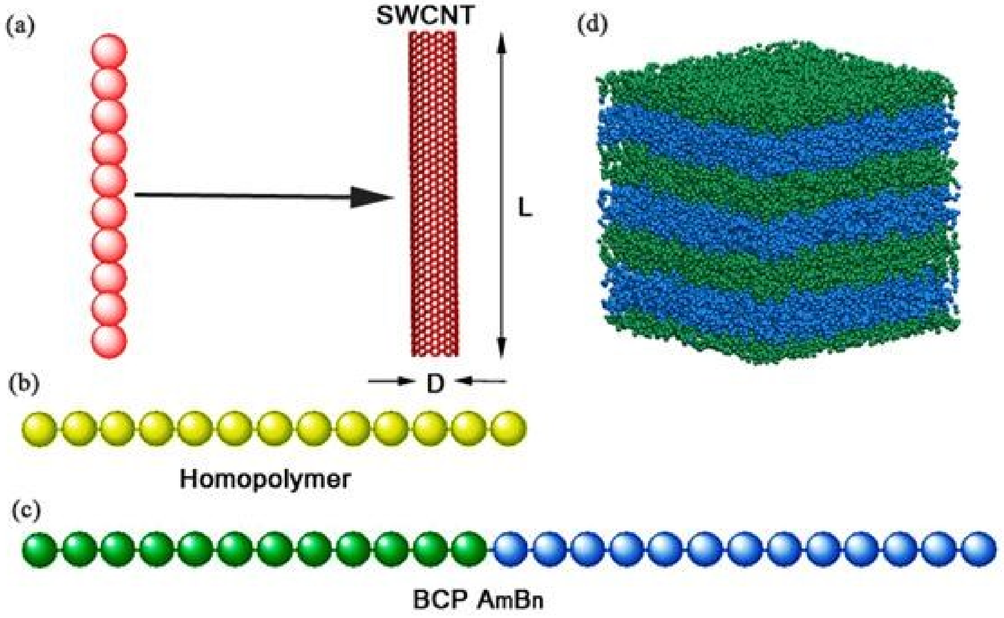

Figure S1 CG model of (a) CNT; (b) Homopolymer chain; (c) symmetric block copolymer chain A_mB_n, with A (green) bead type compatible with CNT. (d) block copolymer template system.

Instead, the CG model homo- and symmetric block copolymer (BCP) there is no bond angle between two consecutive bonds. The CG model of BCP (A_mB_n) (shown in Figure S1 c) is generic but can well represent amphiphilic diblock copolymers such as PMMA-block-PDMS which is similar with that of CNT(10,10). The BPC copolymer (A_mB_n) is noncharged. Block A_m (like PMMA) is hydrophilic and block B_n (like PDMS) is hydrophobic. Furthermore, based on the same bead volume of 740 $Å^3$, one bead represents 188 C atoms (5 PMMA and 7 PDMS beads). Thus, considering a diblock chain with composition $A_{13}B_{12}$ we could rewrite into a block copolymer of $PMMA_{65}$-*b*-$PDMS_{84}$.

Moreover, the χ interaction parameter between CNTs and polymer chains corresponds to some form of the solubility parameter, which is also used in Ref. (1).They employed models of hexagonal and square patterns and simulated the PS_{28}-b-$PDMS_{112}$ polymer chain composed of 140 monomers. The solubility parameter of CNT, PMMA and PDMS is obtained by 18.9 $(J/cm^3)^{1/2}$, 22.7 $(J/cm^3)^{1/2}$, and 9.8 $(J/cm^3)^{1/2}$, respectively[2]. Thus, we could obtain $\chi_{(CNT\text{-}PMMA)}$ x $RT \sim 2.0$ and $\chi_{(CNT\text{-}PDMS)}$ x $RT \sim 10.0$ corresponding to the bead volume of 740 $Å^3$. Considering that, the interaction parameter $\chi_{(CNT\text{-}PMMA)}$ x $RT = 10.0$ kJ mol^{-1} and $\chi_{(CNT\text{-}PDMS)}$ x $RT = 40.0$ kJ mol^{-1}. For the homopolymer a value of $\chi_{(CNT\text{- }HOMOPOLYMER)}$ x $RT = 20.0$ kJ mol^{-1} has been used.

Time coarse-graining scaling factor (τ_{CG}) estimation

The calculated diffusion coefficient from Mean Square Displacement (MSD) of MD-SCF simulation is $D_{Polymer}=1.5 \times 10^{-4}$ cm^2/s for a polymer chain of 20 beads. This value can be compared with experimental (or calculated by atomistic simulations) diffusion data from different polymers having similar chain size. In the case of polystyrene[3] $R_g=2.5$ nm, PS Mw 10.000 (N=100) the diffusion coefficient is $D_{PS}=5\times10^{-8}$ cm^2/s[3]. In this case $\boldsymbol{\tau_{CG}} = D_{Polymer}/D_{PS} \sim 3000$. If we compare *i*-PP the $D_{iPP}=2.4\times10^{-7}$ cm^2/s (*i*-PP melt simulated at 450 K having $N=76$ in Ref. 4). We have $\boldsymbol{\tau_{CG}} = D_{Polymer}/D_{iPP} \sim 800$. For hydrogenated polybutadiene $D_{PB}= 2.0\times10^{-6}$ cm^2/s (N~100 hydrogenated Polybutadiene[4]). In this case $D_{Polymer}/D_{PB} \sim 100$.We have, according to the bulkiness of the repeating units, values of $\boldsymbol{\tau_{CG}}$ ranging from 3000 to 100. So finally we can consider as order of magnitude of the time scaling factor ~1000. According to this the simulations reported in our paper can be considered on the timescale of 1 to 5 milliseconds.

The geometrical percolation of homopolymer melt

The method of geometrical percolation used here is the same with our previous work[5]. The site percolation method as a specific mathematical model is used on a box lattice. This uses an L×L×L box matrix of one and zero, which is called site matrix. One represents an “occupied” site and zero means “empty” site. A cluster composed of CNTs and CB NPs is a set of occupied sites. When all of the occupied sites are connected to an occupied site by neighboring occupied sites. It should be noted that the neighbors are only in the x, y, and z directions, not along the diagonals. If one cluster could go through from above to below, from left to right, or from front to back, the cluster is called spanning cluster. The spanning cluster has an element on both two corresponding surfaces of the site matrix.
A simple algorithm for labeling clusters on a grid was found by J. Hoshen and R. Kopelman[6] in 1976. The Hoshen-Kopelamen algorithm is used to investigate the percolation configurations. They give each site label a another index $b(a)$. As long as a is a “good” label, $b(a)$ is a. But once the cluster labeled with a turns out to be a sub-cluster of a cluster labeled with $c<a$, $b(a)$ is set to c. By traversing the resulting tree structure up to the root label, the “good” label for each cluster site can be found. The sites are occupied randomly with some site occupation probability, P.
In our system, the percolation probability is obtained by average several configurations after the system reaches the equilibrium. Moreover, the averaged value from three parallel simulation runs is obtained to describe the percolation probability correctly.

The results indicate that there is lower percolation threshold in the nanocomposites with the longer CNT, which is agreement with the experimental results. The percolation threshold is about 12.0 vol% (aspect ratio of CNT 10.6), 3.0 vol% (aspect ratio of CNT 20.2), and 2.5 vol% (aspect ratio of CNT 10.6), respectively.

The energy potential of systems BTCR and BTCO

The potential energy curves corresponding to the simulation time for three different processing methods are shown in Figure 8 for the system BRCR and in Figure S2 for systems BTCR and BTCO.

For the system of BTCR, CNTs are generated randomly in the BCP template at the beginning of the simulation. At 2×10^6 steps, CNTs form into larger bundles firstly in the same block due to Van der Waals’ force. Increasing the simulation time into 2×10^7 steps, CNT continues to aggregate into larger bundles that are not only in the plane of block A phase, but also come through the z direction of the template. Moreover, CNT prefers to stay in the interface of the two blocks to decrease the surface energy. Increasing the simulation time continuously after 5×10^7 steps, the potential energy is stable and the morphologies of CNTs and BCP template are not changed. Thus, the simulation time of 7×10^7 steps is suitable for BTCR system to reach the equilibrium.

For the system of BTCO, CNT distributes initially and randomly in the block A of BCP template. During the self-assembly of BCP template and CNT, CNT aggregates into bundles only in the block A phase and percolated clusters are also formed in the block A phase. Through the comparison of the self-assembled morphologies at 3.3×10^7 steps, 4.3×10^7 steps, and 5×10^7 steps, we could make sure that the simulation time of 5×10^7 steps is long enough to make the system reach the equilibrium.

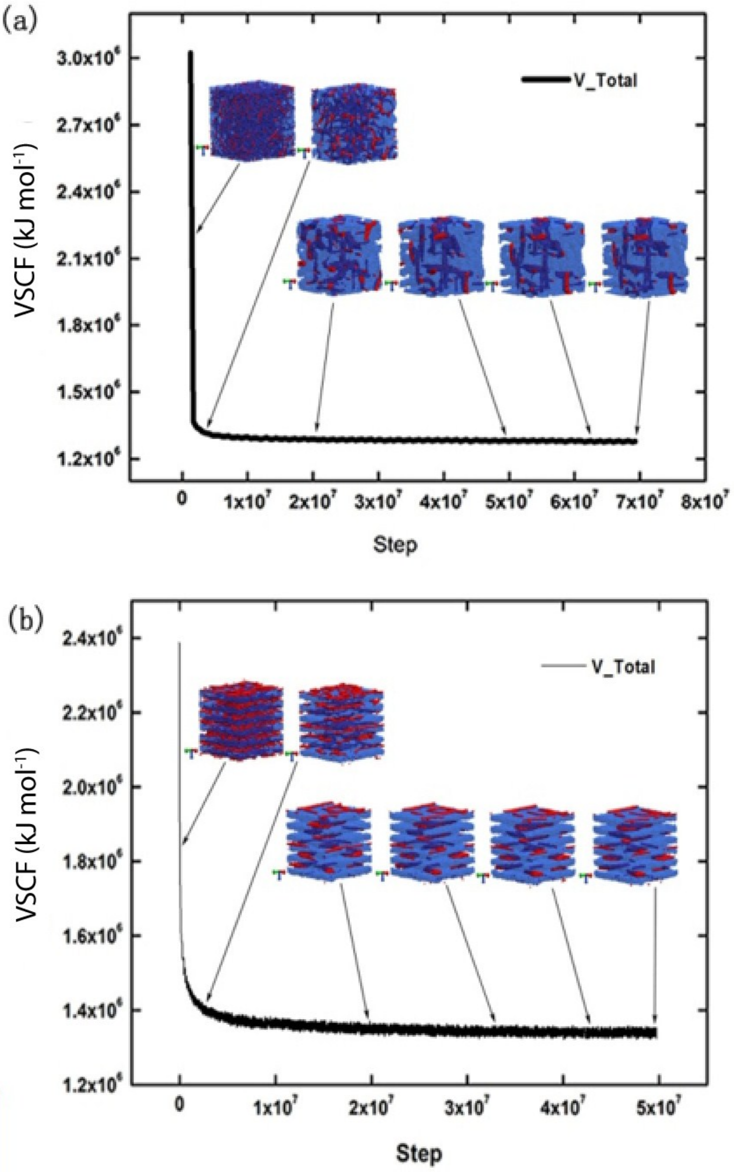

Figure S2. Time behaviour of VSCF potential for the systems: (a) BTCR, (b) BTCO.

Table S1. Simulation details of nanocomposites self-assembled from Homopolymer and CNT.

System	Aspect Ratio CNT	No. Particles of one CNT	CNT Length [nm]	Box Length [nm]	No. Total Particles	Vol% CNT (*)	Simulated time [steps]
HCR1	10.6	13	14.84	113.12	437,840	1.0%～20.0%	$1.8\times10^{7(A)}$
HCR2	20.2	25	28.28	113.12	440,000	1.0%～10.0%	$1.8\times10^{7(B)}$
HCR3	30.6	38	42.84	171.36	1,529,994	0.5%～2.0%	$5.2\times10^{7(C)}$

* for each system 10 different CNT compositions have been simulated. More information are reported in Table S1 of Supporting Information Section.

Table S2. Simulation details of nanocomposites self-assembled from BCP and CNT.

System	Mixing method (initial configuration)	Aspect Ratio CNT	No. Particles of one CNT	CNT Length [nm]	Box Length [nm]	Vol% CNT (*)	Simulated time [steps]
BRCR	BCP and CNT randomly dist.	20.2	25	28.28	113.12	1.0%〜8.0%	$1.6\times10^{8(A)}$
BTCR	BCP template and CNT randomly dist.	20.2	25	28.28	113.12	1.0%〜8.0%	$7\times10^{7(B)}$
BTCO	BCP template and CNT in compatible block	20.2	25	28.28	171.36	0.5%〜8.0%	$5\times10^{7(C)}$

* for each system have been simulated 8 different CNT conc. The system compositions are reported in Table S2 of Supporting Information Section.

Considering the time scaling factor τ_{CG}, the total time of simulations are: (A) 4.8 ms, (B) 2.1 ms, (C) 1.5 ms.

Table S3. Simulation composition for HCR1, HCR2, and HCR3 systems.

Vol %	HCR1			HCR2			HCR3		
	CNT	Homo-polymer	Total Part.	CNT	Homo-polymer	No. Total Part.	CNT	Homo-polymer	Total Part.
1	4,368	433,472	437,840	4,400	435,600	440,000	15,314	1,514,680	1,529,994
2	8,762	429,078	437,840	8,800	431,200	440,000	30,590	1,499,404	1,529,994
3	13,130	424,710	437,840	13,200	426,800	440,000	45,904	1,484,090	1,529,994
4	17,511	420,329	437,840	17,600	422,400	440,000	61,180	1,468,814	1,529,994
5	21,892	415,948	437,840	22,000	418,000	440,000	76,494	1,453,500	1,529,994
6	26,273	411,567	437,840	26,400	413,600	440,000	91,808	1,438,186	1,529,994
7	30,654	407,186	437,840	30,800	409,200	440,000	107,100	1,422,894	1,529,994
8	35,022	402,818	437,840	35,200	404,800	440,000	122,400	1,407,594	1,529,994
9	39,403	398,437	437,840	39,600	400,400	440,000	137,699	1,392,295	1,529,994
10	43,784	394,056	437,840	44,000	396,000	440,000	152,999	1,376,995	1,529,994

Table S4. Simulation composition of BRCR, BTCR, and BTCO systems.

Vol%	No. CNT	No. BCP	No. Total Particles	Box Length [nm]
1	4,425	438,000	442,425	113.51
2	8,950	438,000	446,950	113.90
3	13,550	438,000	451,550	114.29
4	18,250	438,000	456,250	114.68
5	23,050	438,000	461,050	115.08
6	27,950	438,000	465,950	115.49
7	32,975	438,000	470,975	115.90
8	38,100	438,000	476,100	116.32

Reference

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