Supporting Information

Self-Assembled Morphologies and Percolation Probability of Mixed Carbon Fillers in the Diblock Copolymer Template: Hybrid Particle-Field Molecular Dynamics Simulation

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Coarse-grain models and parameters

CG model for SWCNT (10,10) with the diameter σ of 1.4 nm, and bonds between two successive particles are described with the equilibrium distance of 0.8×σ =1.12 nm. Thus, according to the equation (1),

$$V_{bead} = \frac{4}{3}\pi r^3 \qquad (1)$$

we could roughly obtain the volume of one bead is 740 $Å^3$ and it represents 188 C atoms. Furthermore, the CG model of BCP $A_{12}B_{13}$ is generic, but can represent amphiphilic diblock copolymers such as PMMA-*b*-PDMS. According to the molecular weight and the experimental bulk densities of the polymer, the monomer volumes are calculated and shown in Table S1. Therefore, block copolymer $A_{12}B_{13}$ could represent $PMMA_{60}$-*b*-$PDMS_{65}$ of 125 repeat units. This evaluation of CG model size is agreement with other CG simulations, for example, A_2B_8 reprensents PS_{28}-*b*-$PDMS_{112}$ of 140 repeat units in Ref. 1.

Table S1 Molecular parameters of polymer. The monomer volumes are calculated using the molecular weight and the experimental bulk densities.

Polymer	Molecular Weight *M*(g/mol)	Density (g/cm^3)	Monomer Volume($Å^3$)	Monomer number per bead
PMMA	100	1.19	140	5
PDMS	90	1.0	150	5

Moreover, the interaction parameter of SWCNT(10,10) and CG polymer chains correspond to some form of the solubility parameters, which is also used in Ref. 1. The solubility parameter of SWCNT, PMMA, and PDMS is obtained by 18.9 $(J/cm^3)^{1/2}$, 22.7 $(J/cm^3)^{1/2}$, and approximately 10.0 $(J/cm^3)^{1/2}$ (considering the influence

such as temperature and solvent compatibility[2]), respectively[3]. Actually, the solubility parameter δ is the square root of the cohesive energy density. The Flory-Huggins χ parameter can be calculated from the solubility parameters by the equation (2)

$$\chi_{12} = \frac{V_{\text{bead}}}{k_{\text{B}}\text{T}}(\delta_1 - \delta_2)^2 \qquad (2)$$

Where V_{bead} is the volume of the bead size of CG model. Thus, we could calculate $\chi(SWCNT(10,10) - PMMA) \approx 2.0$, $\chi(SWCNT(10,10) - PDMS) \approx 10.0$ and $\chi(PMMA - PDMS) \approx 10.0$ corresponding to the bead volume of 740 Å^3. This parameter choice related to Flory-Huggins parameters according to the representation of monomer size per CG segment is the same with the Ref. 1.

At last, in the hybrid particle-field MD-SCF simulation, $\chi(RT)$ with the unit of $\text{kJ}\cdot\text{mol}^{-1}$ is used in program OCCAM. Finally, interaction parameters $\chi(SWCNT(10,10) - PMMA) \approx 10.0$ $\text{kJ}\cdot\text{mol}^{-1}$, $\chi(SWCNT(10,10) - PDMS) \approx 40.0$ $\text{kJ}\cdot\text{mol}^{-1}$, and $\chi(PMMA - PDMS) \approx 40.0$ $\text{kJ}\cdot\text{mol}^{-1}$ are used in the hybrid particle-field MD-SCF simulation.

The validation of CG Models

In order to validate the CG models, we choose three different systems to test, including (1) SWCNT(10,10) and homopolymer PMMA with the 4.0 vol% SWCNT(10,10); (2) SWCNT(10,10) and homoplymer PDMS with 4.0 vol% SWCNT(10,10); (3) PMMA-*b*-PDMS. The details of three simulation systems are show in Table S2.

The equilibrium morphologies of homopolymer-SWCNT (10,10) composites are shown in Figure S1, which corresponds to simulation time of 360 ns. For the system

Table S2 The details of systems in the MD-SCF simulations.

System	$\chi(RT)$ (kJ·mol^{-1})	Length of SWCNT(10,10)	Length of polymer
SWCNT(10,10) and PMMA	10.0	13	13
SWCNT(10,10) and PDMS	40.0	13	13
PMMA-*b*-PDMS	40.0	0	25

of SWCNT(10,10) and homopolymer PMMA, Figure S1(a) and (b) shows that the SWCNT well disperse into the homopolymer PMMA and loose network is formed, which agrees well with the experiments[4]. Furthermore, Figure S1(c) and (d) shows that highly entangled SWCNT bundles by van der Waals attraction force are embedded in the homopolymer PDMS, which are the same with the experimental observations[5].

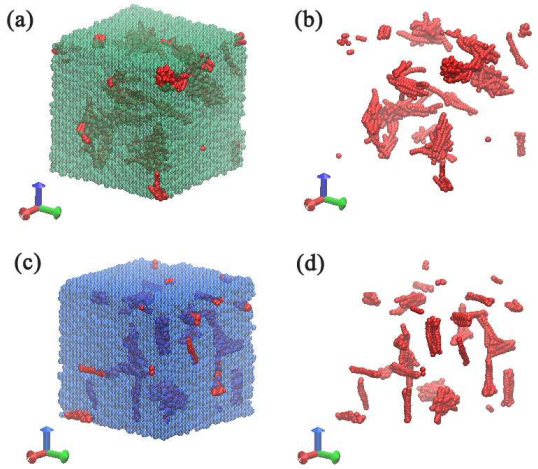

Figure S1. Equilibrium morphologies of homopolymer-SWCNT (10,10) composites. (a) homopolymer PMMA in green and SWCNT(10,10) in red; (b) dispersed SWCNT(10,10) in hompolymer PMMA; (c) homopolymer PDMS in blue and SWCNT(10,10) in red; (d) dispersed SWCNT(10,10) in homopolyer PDMS.

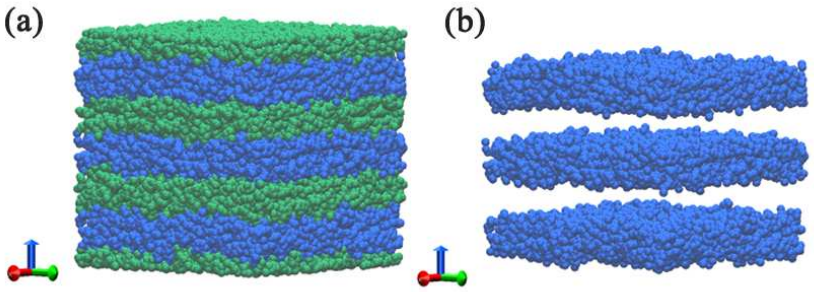

Figure S2. Equilibrium morphologies of block copolymer $PMMA_{60}$-*b*-$PDMS_{65}$. (a) block PMMA in green and block PDMS in blue; (b) block PDMS in blue.

Correspondingly, the equilibrium morphology of $PMMA_{60}$-*b*-$PDMS_{65}$ are shown in Figure S2. The lamellar phase is formed from $PMMA_{60}$-*b*-$PDMS_{65}$, which agrees well with the experimental results in Ref. 6.

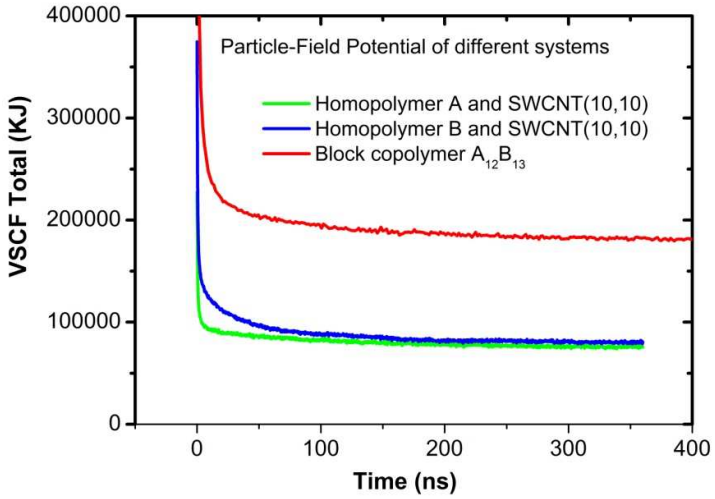

Figure S3. The Particle-Field potential energy of three different systems corresponds to the simulation time. Green line represents the system of homopolymer PMMA and SWCNT(10,10); blue line represents the system of homopolymer PDMS and SWCNT(10,10); and red line represents the system of block copolymer $PMMA_{60}$-*b*-$PDMS_{65}$.

Finally, the particle-field potential energy of three different systems corresponds

to the simulation time are calculated and shown in Figure S3. The lowest energy curve line in green corresponds to the system of SWCNT(10,10) in homopolymer PMMA with the smallest interaction parameter $\chi(RT)$=10.0 kJ·mol^{-1}. The higher energy curve line is in blue, which represents the system of SWCNT(10,10) in homopolymer PDMS with the interaction parameter of 40.0 kJ·mol^{-1}. At last, the red line of block copolymer $PMMA_{60}$-*b*-$PDMS_{65}$ has the highest energy curve line due to the high interaction and bond connection between block PMMA and block PDMS.

References:

(1) Feng, J.; Cavicchi, K. A.; Heinz, H., Control over Self-Assembly of Diblock Copolymers on Hexagonal and Square Templates for High Area Density Circuit Boards. *ACS Nano* **2011**, *5*, 9413-9420.

(2) Lee, JN.; Park, C.; Whitesides, GM., Solvent Compatibility of Poly(dimethylsiloxane)-Based Microfludic Devices. *Anal. Chem.* **2003**, *75*, 6544-6554.

(3) Maiti, A.; Wescott, J.; Kung, P., Nanotube-Polymer Composites: Insights from Flory-Huggins Theory and Mesoscale Simulations. *Molecular Simulation* **2005**, *31*, 143-149.

(4) Lahelin, M.; Annala, M.; and Nykänen, A. et al., In Situ Polymerized Nanocomposites: Polystyrene/CNT and Poly(methyl methacrylate)/CNT composites. *Compos. Sci. Technol.* **2011**, *71*, 900-907.

(5) Cao, H.; Gan, Z.; and Lv, Q. et al., Single-Walled Carbon Nanotube Network/Poly Composite Thin Film For Flow Sensor, *Microsyst. Technol.* **2010**, *16*, 955-959.

(6) Luo, Y.; Montarnal, D.; Kim, S. et al. Poly(dimethylsiloxane-*b*-methylmethacrylate): A Promising Candidate for Sub-10 nm Patterning, *Macromolecules,* **2015**, *48*, 3422-3430.