Supporting Information

Exploring Thermodynamic and Structural Properties of Carbon Nanotube/Thermoplastic Polyurethane Nanocomposites from Atomistic Molecular Dynamics Simulations

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Number of Figures: 3

Contents

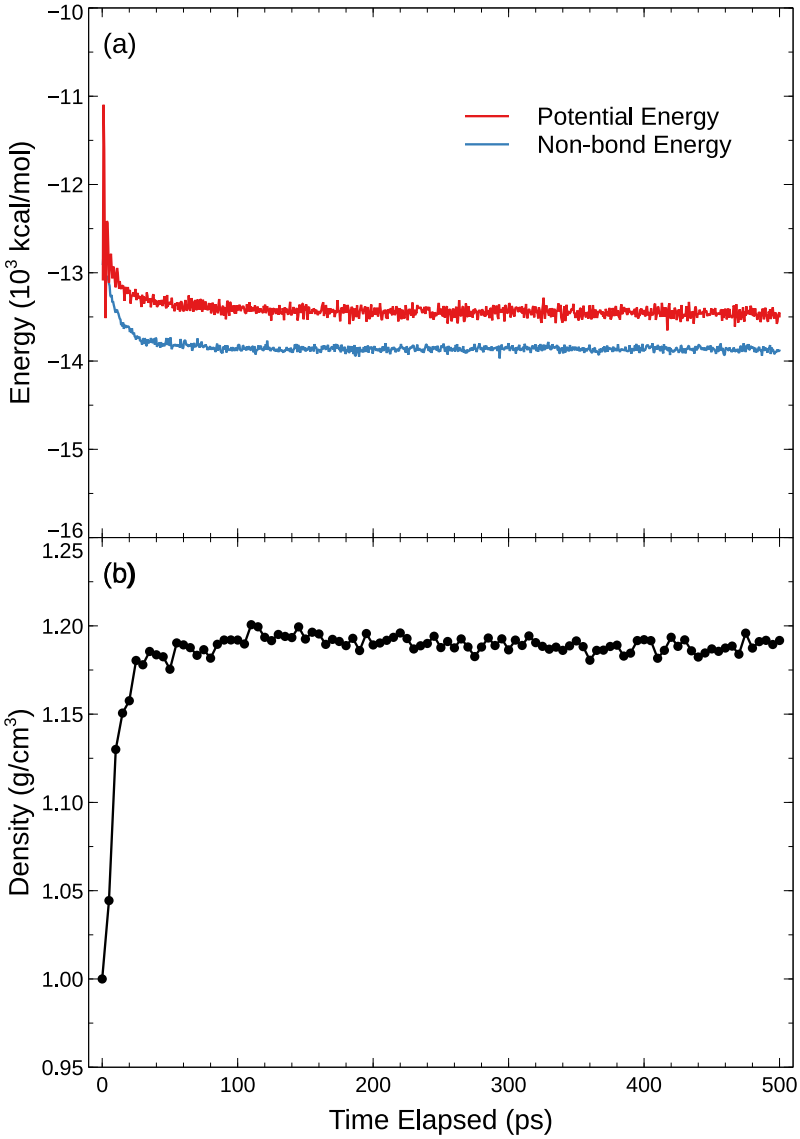

Figure S1: The changes of (a) system energies and (b) density with the simulation time at the first 500 ps.

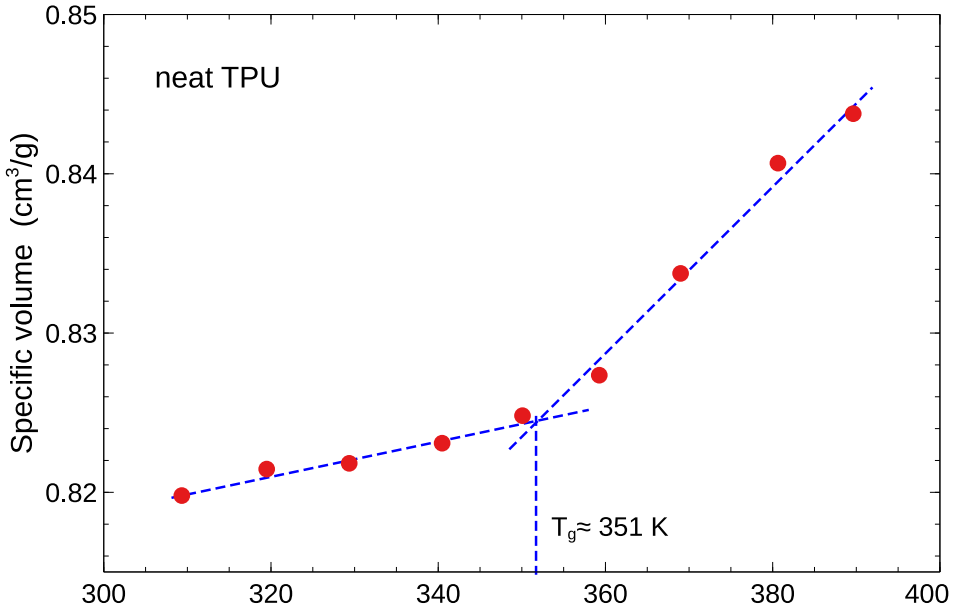

Figure S2: The glass transition temperature T_g for pure TPU is determined through the specific volume vs. temperature.

Solubility parameter

An alternative approach to evaluate the SWNT/TPU interaction strength is the cohesive energy density (CED) and the solubility parameter. The CED measures the total inter-molecular interactions of materials per unit volume, including the electrostatic and van der Waals contributions. The Hildebrand solubility parameter, δ, is defined as the square root of the cohesive energy density, which is mathematically described by

$$\delta = \sqrt{\text{CED}} = \sqrt{\frac{E_{\text{cov}}}{V}} \tag{1}$$

, where E_{cov} is the internal energy change during vaporization, namely the energy required to separate all molecules. In this work, ΔH_{cov} can be computed by averaging all the inter-molecular non-bonded energy over simulation time,[1,2] as follows,

$$\delta_{\text{total}} = \sqrt{-\frac{\left\langle \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} E_{i,j} \right\rangle}{\langle V \rangle}} \tag{2}$$

, where $E_{i,j}$ is the total non-bond energy between molecule i and j, V is the volume of simulation box, and $\langle\rangle$ indicates a time average over the MD simulation time. Moreover, the total inter-molecular potential energy can be segmented into van der Waals and electrostatic parts, allowing the energy contributions from van der Waals (δ_{vdw}) and electrostatic ($\delta_{\text{electrostatic}}$) interactions to be considered separately, similar to the Hansan solubility parameter.[3]

Through our MD simulations, the δ_{total}, δ_{vdw}, and $\delta_{\text{electrostatic}}$ for neat TPU are found to be approximately 22.93, 19.68, and 10.84 $\text{MPa}^{0.5}$, respectively. According to literature,[4] the δ_{total}, δ_{vdw}, and $\delta_{\text{electrostatic}}$ for SWNTs are estimated as 20.80, 19.4, and 7.5 $\text{MPa}^{0.5}$, respectively. By comparing the corresponding solubility parameters, it is inferred that the bad compatibility between SWNTs and TPUs originates mostly from a mismatch of electrostatic interactions between them. To properly measure the contributions of functional groups to SWNT-TPU interfacial interactions, the solubility parameters of functionalized

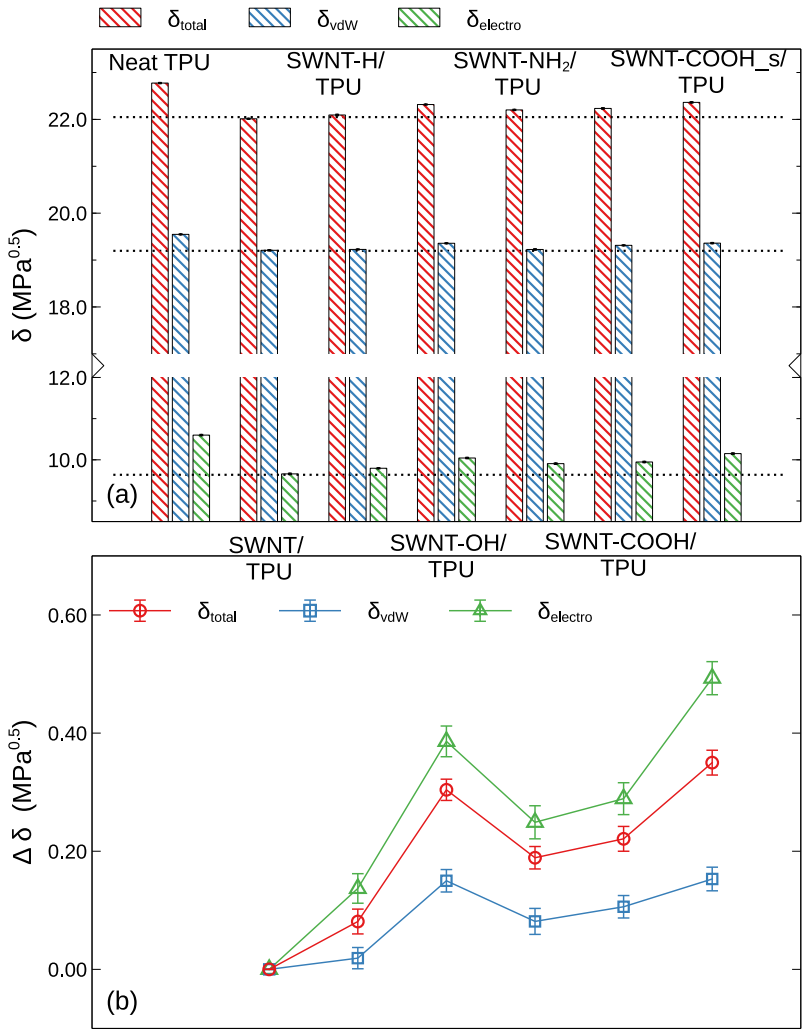

Figure S3: (a) The Hildebrand solubility parameter δ_{total}, the van de Waals and electrostatic contributions to the solubility parameters. (b) $\Delta\delta$, the difference between the δ of the functionalized SWNT/TPU system and the pristine SWNT/TPU system.

SWNTs/TPU composites are compared to that of pristine SWNT/TPU system, as stronger interfacial binding energy leads to higher CEDs and consequently larger solubility parameters. From Fig. S3a, the functionalized SWNT-filled composite systems are seen to have larger δ_{total} than the pristine SWNT/TPU system, attributed to the interactions between functional groups with TPU molecules. Therefore, the difference between the δ of the functionalized SWNT/TPU system and the pristine SWNT/TPU system, $\Delta\delta$, is further calculated to quantify the contributions of functional groups. By comparison (Fig. S3b), it is demonstrated once more that the van der Waals interactions exert minor influence to the

functionalized SWNT/TPU interface, while the electrostatic interactions dominate the interfacial characteristics, as indicated by the much higher $\Delta\delta_{\text{electrostatic}}$ than $\Delta\delta_{\text{vdW}}$ for those TPU nanocomposites filled with polar groups-modified SWNTs (-OH, -NH_2, and -COOH).

References

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