Electronic supplementary information

Molecular dynamics simulations of the effects of carbon nanotube content on stretch-induced crystallization of polyethylene/carbon nanotube nanocomposites

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Model and simulation method

The force field of Paul et al. was used for the current simulations of PE chains[1]. In this force field, E_{total} (the total potential energy of the system) can be given as follows:

$$E_{total} = E_{bond} + E_{angle} + E_{torsion} + E_{vdW}$$

The detail descriptions of E_{bond}, E_{angle}, $E_{torsion}$ and E_{vdW} can be seen in Table S1.

Table S1. The form field and potential parameters for molecular dynamics simulation of PE.

The potential energy	Potential function	Values/Units
Bond stretching energy	$E_{bond} = K_l(l - l_0)^2$	K_l=350kcal/mol, l_0= 1.53Å
Bond angle bending energy	$E_{angle} = K_\theta(\theta - \theta_0)^2$	K_θ=60kcal/mol Å^{-2}, θ_0=109°
Dihedral angular torsional potential energy	$E_{torsion} = \sum_{n=1}^{3} K_n[1 - cos(n\emptyset)]$	K_1=0.81kcal/mol, K_2=0.43kcal/mol, K_3=1.62kcal/mol

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| Nonbonded interaction energy | $E_{vdW} = 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right]$ | ε=0.112kcal/mol, σ= 4.01 Å, $r \leq r_c$ |

In the current simulations, the adaptive intermolecular reactive empirical bond-order (AIREBO) potential function was used to describe the atomic interaction between CNTs. If the force field of Paul et al. was used to reflect the interaction between CNTs instead of the reactive force field, the CNTs would break during the stretching process, as show in Figure S1.
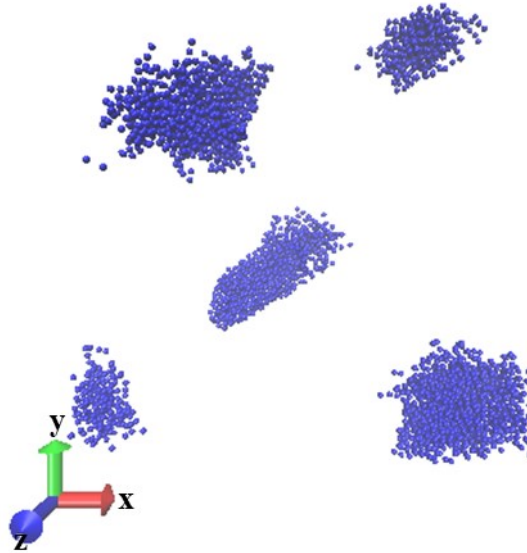

Fig. S1. Snapshot of L73-4 system at the initial state of stretching.

Definition of structure parameters

The method proposed by Yang et al. was used to define and calculate crystallinity of polymers [2]. Yang et al. defined a Site Order Parameter (SOP), which was used to obtain the local order parameters of the bond vectors around a particular atom within a certain local region. The SOP of the kth atom (the total number of k sites corresponds

to the total number of PE atoms) within a local region with the radius of R is expressed as

$$SOP_k = \frac{\langle 3COS^2(\Phi) - 1 \rangle}{2} = \frac{3}{2}\langle (\vec{e}_i \cdot \vec{e}_j)^2 \rangle_R - \frac{1}{2}$$

where $\vec{e}_i$ and $\vec{e}_j$ are two bond vectors located around the ith and jth atoms, respectively, and Φ is the angle between $\vec{e}_i$ and $\vec{e}_j$. For instance, $\vec{e}_i$ is expressed as the vector from atom i-1 to atom i+1. The radius of the local region around a particular atom for the SOP calculation is selected as 5.5 Å. This selection of the radius value is determined by the position of the disappearance of the first adjacent peak in the radial distribution function. According to the previous experience, the threshold value for the crystallinity calculation is set as 0.7. When SOP_k is greater than 0.7, the corresponding center atom is considered to be in crystalline regions. Then, the crystals are just formed by these crystalline atoms. Furthermore, the ratio of these atoms in the crystalline regions to the total number of atoms is defined as crystallinity (X_c), which can be defined as follows:

$$X_c = \frac{N_c}{N_a}$$

where N_c is the number of PE atoms with the SOP_k higher than 0.7, and N_a is the total number of PE atoms in the corresponding system.

In order to obtain the value of the relaxation time, the mean-squared displacement of the center of mass of polymer chains ($g_3(t)$) was calculated, as shown in Fig. S2 of the Supporting Information. Then, the relaxation time (Rouse time) can be obtained at the value ($\tau_R = 5.78$ ns) when $g_3(\tau_R) = \langle R_g^2 \rangle$.
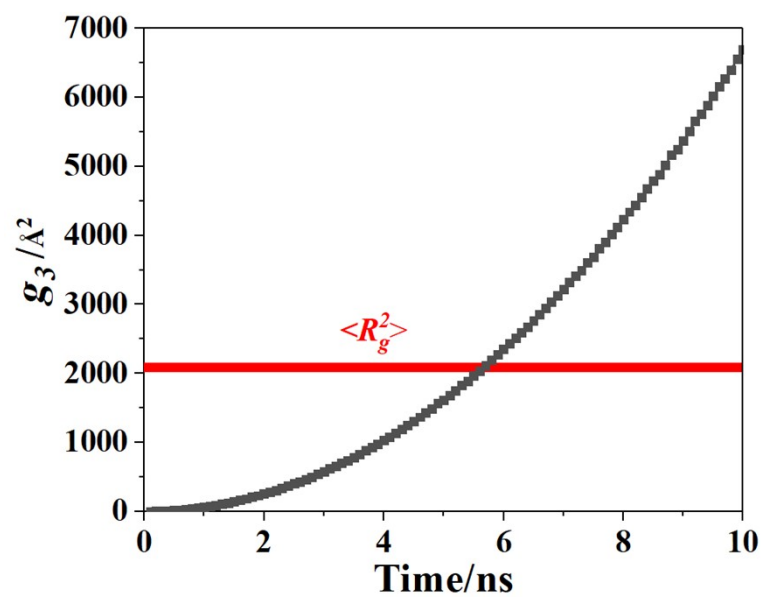
Fig. S2 Evolution of mean-squared displacement of the center of mass of PE chains during relaxation at $T = 600$ K.
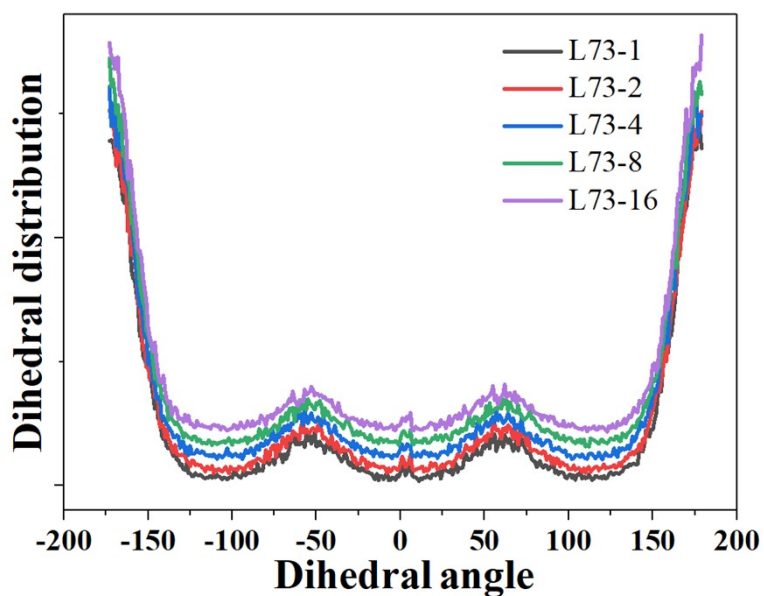

Fig. S3 The average distributions of the values of the chain dihedral angles for the different filled systems. For clarity, the corresponding curves were translated in the vertical direction.
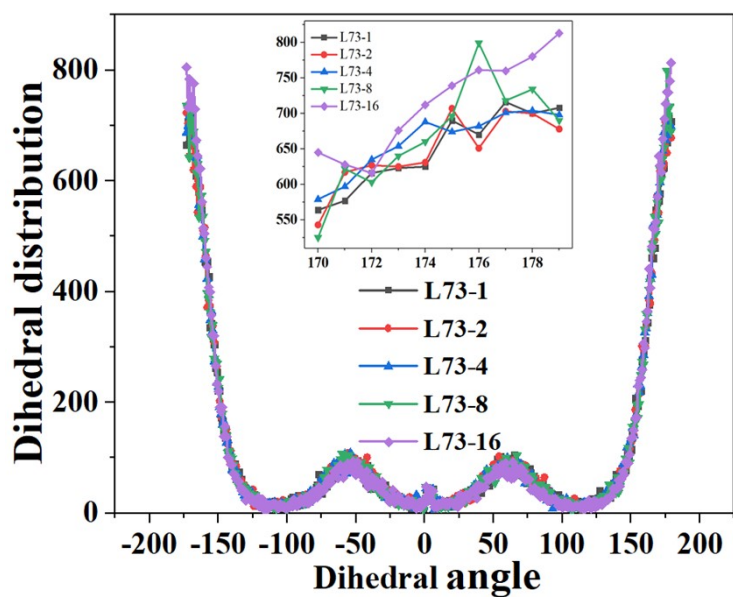
Fig. S4 The distribution of the values of the dihedral angles in the different filled systems at strain of 0; the inset shows the distribution of the dihedral angles in the local region.
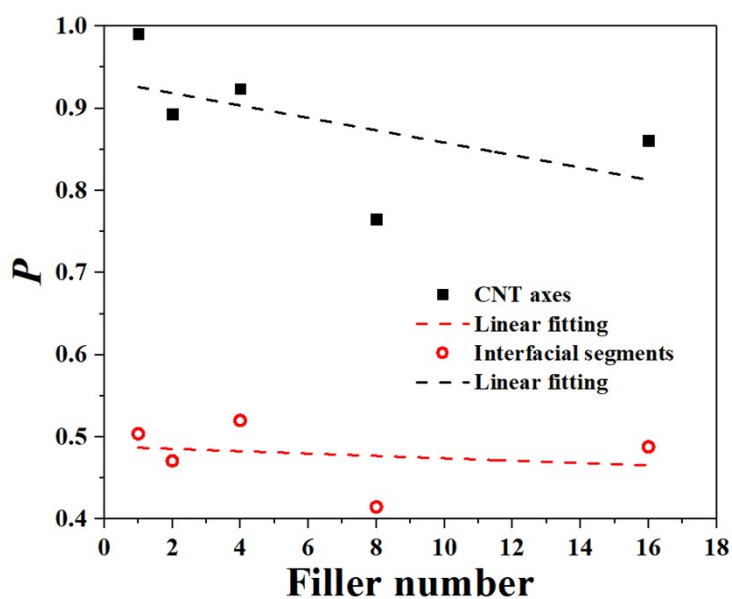

Fig. S5 Orientational-order parameters (*P*) of the CNT axes along the stretching direction and the interfacial segments along the CNT axes as a function of the filler number. The dash lines represent the linear fitting of the dependences of the corresponding orientational-order parameters on the filler number. These data were obtained in the different filled systems at strain of 3 and temperature of 600 K.
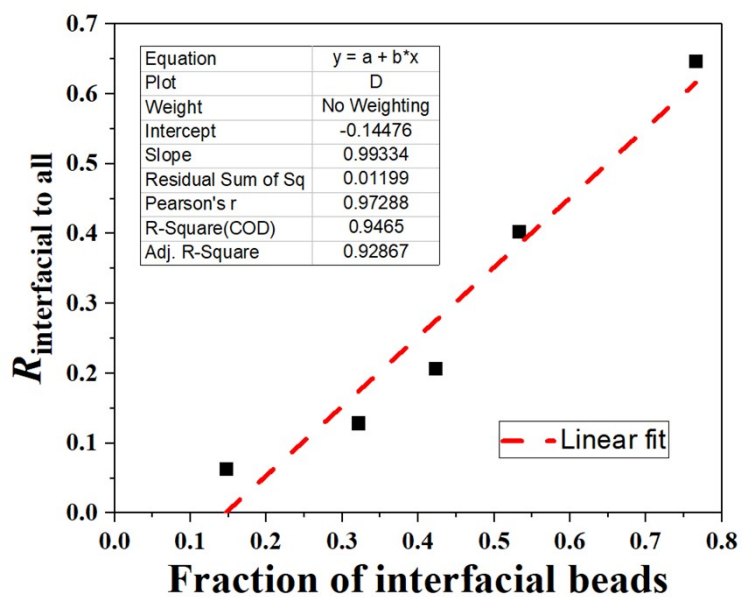
Equation	y = a + b*x
Plot	D
Weight	No Weighting
Intercept	-0.14476
Slope	0.99334
Residual Sum of Sq	0.01199
Pearson's r	0.97288
R-Square(COD)	0.9465
Adj. R-Square	0.92867

Fig. S6 The ratio of the precursor contents in the interfacial regions to the contents of all precursors in the systems as a function of the fraction of the polymer beads in the interfacial regions.
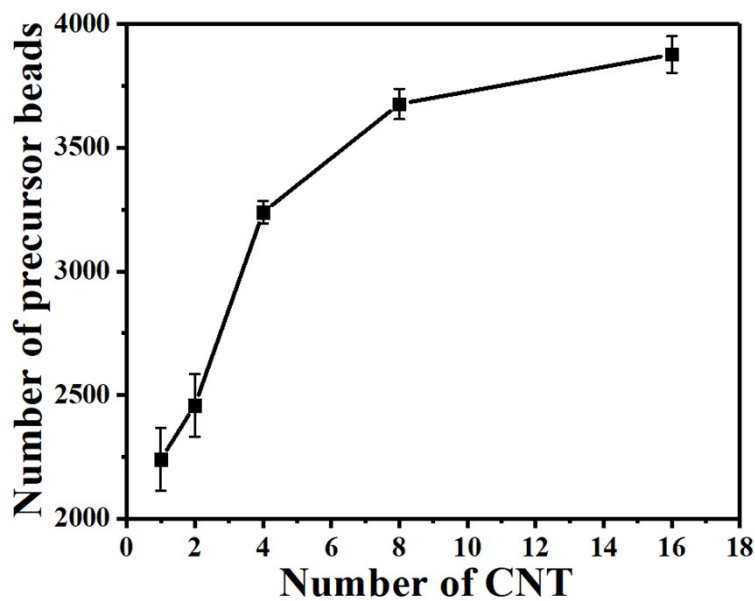

Fig. S7 Number of precursor beads in systems with different numbers of CNTs at the strain of 3.
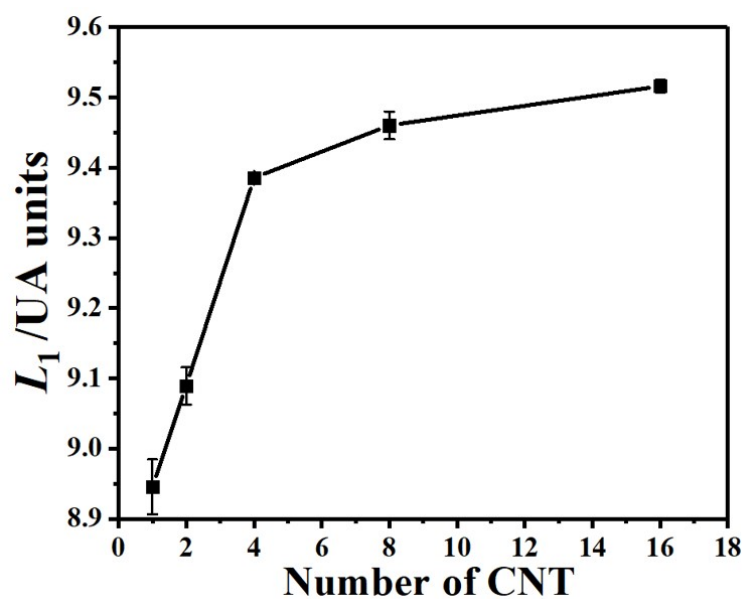
Fig. S8 Average length of all-*trans* conformational segments in systems with different numbers of CNTs.
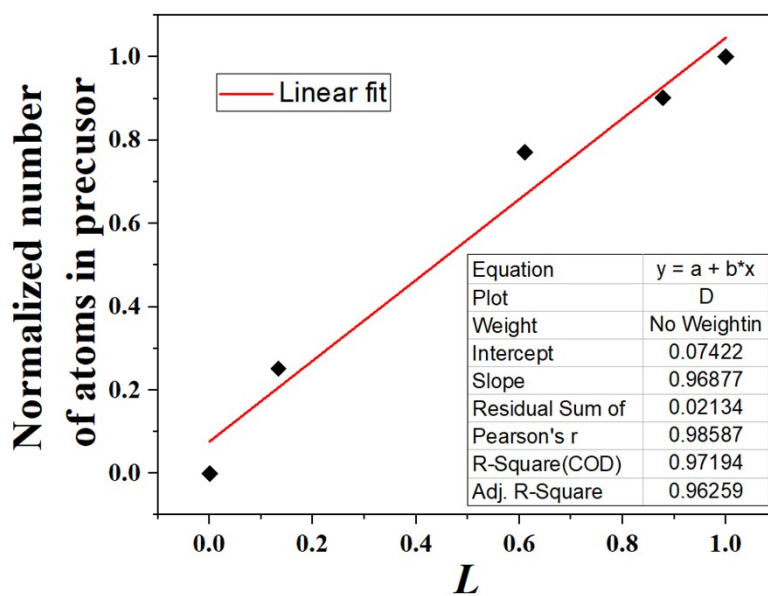

Fig. S9 The normalized number of atoms in precursors as a function of the normalized average length of all-*trans* conformational segments.
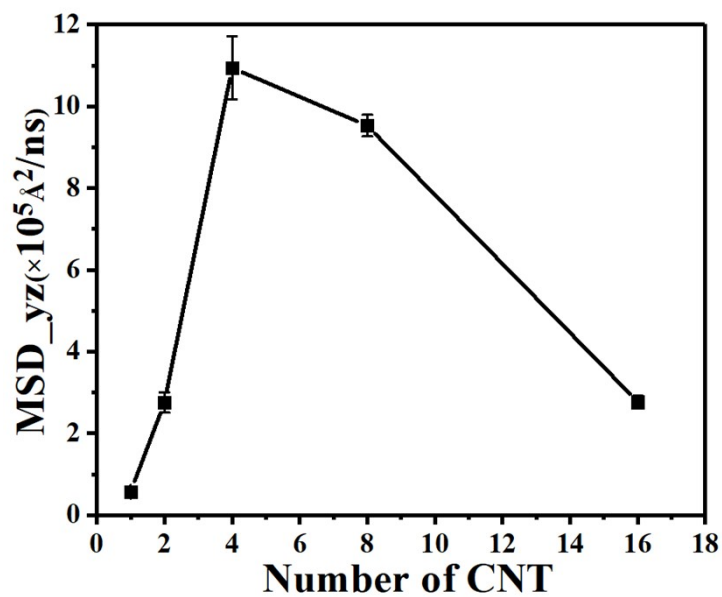
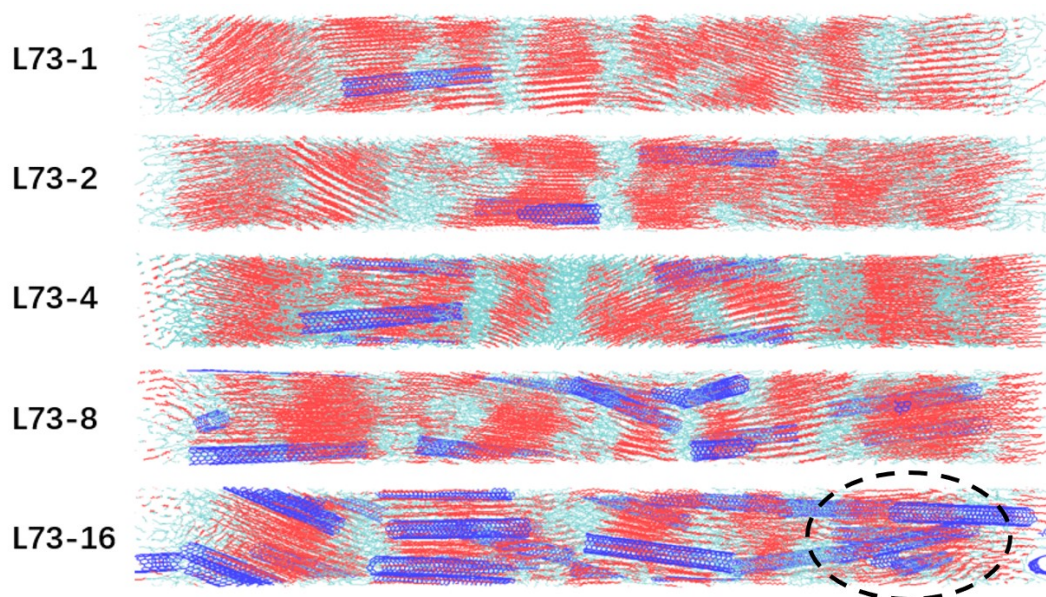**Fig. S10** MSD of polymer beads within 1 ns in the yz plane.

Fig. S11 Snapshots of the filled systems with the different CNT contents at the end of isothermal crystallization; the red lines denote the crystalline stems, and the sky-blue lines denote the amorphous segments. (Supplementary Information)

References

[1] W. Paul, D. Y. Yoon, G. D. Smith, *J. Chem. Phys.*, 1995, **103**, 1702-1709.

[2] X. Yu, B. Kong, X. Yang, *Macromolecules*, 2008, **41**, 6733-6740.