

Ultralow CNT-Reinforced Phase-Change Fibers for Scalable Wearable Thermoregulation

Corresponding Author: Professor Ruqiang Zou

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript introduces a nanotechnology-inspired strategy that combines ultralow CNT (0.1 wt.%) heterostructures with gradient crystallinity engineering to produce scalable PCFs, and these fibers exhibit exceptional synergy between thermal storage density and adaptive thermal regulation capabilities. The integrated experimental and MD studies elucidate three synergistic strategies to optimize PCFs performance: 3D-IPNs confinement engineering, CNT-induced structural modulation, and a scalable manufacturing paradigm. Furthermore, these fibers can be cut and sewing to PCM-based thermoregulatory clothing that outperforms traditional polyester fabrics in thermal regulation, maintaining stable thermal conditions under dynamic environmental temperatures, while demonstrating transformative potential for wearable systems in extreme-environment applications and medical thermotherapy applications. Overall, the methodology is reasonable and logical. Below are a few comments on your manuscript.

1. In this manuscript, authors obtained C22/CNT fibers from primary fibers that underwent 3 stretching cycles, so how to balance the relationship between the number of stretching cycles and mechanical properties of fibers? Will increasing the number of stretching cycles further enhance the final mechanical properties of the fibers?
2. On line 207 of page 9, "single-roll C22/CNT3 fibers (with a diameter of 200 mm and inner width of 56 mm)", the diameter should be length.
3. On line 335 of page 13, "Free energy analysis revealed that CNT-induced nucleation barrier reductions in nucleation barriers were attributed to decreases in interfacial energy and strain energy minimization", could the author further visually demonstrate how the interfacial energy and strain energy changes?
4. Please check the reference citation format in the manuscript, for example, line 355 of page 15.
5. Part of the description in Fig. 4 shows unclear font display. Additionally, what stage is the RDF distribution in Fig. 4i?
6. What is the set stress strain rate in MD simulation? Is there any experimental verification?
7. In the supporting documents, I think that the introduction to the subsections in section 1.6 is redundant. Additionally, relevant references and reasons should be provided for the rationality of the selection of the force field.

Reviewer #2

(Remarks to the Author)

The manuscript reports phase-change fibers by incorporating ultralow CNT loading into an interpenetrating polymer network (HDPE/SEBS). The authors demonstrate high latent heat storage, enhanced mechanical robustness, and improved thermal conductivity in the fiber. The work is interesting, combining experiments and molecular dynamics simulations, and demonstrates potential applications in wearable thermal management. However, there are several concerns that should be addressed before the manuscript can be considered for publication.

1. In Fig. 2c, the authors assign the observed lattice spacing of 0.32 nm to the HDPE. Could the authors clarify which crystallographic plane of it corresponds to? The reported d spacing is 0.32 nm, but the (110) and (200) plane of orthorhombic PE have strong diffraction at d-spacings of around 0.41 nm and 0.37nm, respectively (e.g., Polymer, 2021, 212: 123164.). Is it possible to be something else?
2. The MD simulations in Fig. 3 focus on the interaction between n-docosane and CNTs, which demonstrates the heterogeneous nucleation and crystallization behavior. However, the actual fiber system also contains HDPE and SEBS, which may significantly influence molecular confinement and crystallization dynamics. Could the authors explain why these polymer components were not included in the simulations, and discuss whether this might limit the accuracy or

completeness of the MD interpretation?

3. The manuscript claims that the melt-spinning and multi-stage stretching processes largely influence chain orientation and crystallization behavior of the fibers. However, the DSC analysis only compares fibers with different CNT loadings, without showing the thermal response of the unspun precursor and the fibers without stretching. Including a comparison of enthalpy before and after spinning and stretching would strengthen the mechanistic interpretation.

4. While the manuscript claims 0.1 wt.% CNT as the optimal loading for performance (thermal stability, latent heat, and mechanical strength), the orientation degree (Fig. 4d) and elongation at break (Fig. 4b) are highest with 0.05 wt.% CNT. It would be helpful if the authors could further discuss why the optimal CNT content differs depending on the performance metric.

5. There are some typos and grammatical errors (e.g., “blew 40%” should be “below 40%”). In addition, the fonts in some figures are too small (e.g., Fig 4a-d, etc.).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have carefully read the authors' responses and the revised manuscript. In my view, the main concerns raised in my previous report have been adequately addressed, and the presentation has been significantly improved. I therefore consider the manuscript suitable for publication in its present form.

Reviewer #2

(Remarks to the Author)

My concerns were addressed, and the manuscript quality is enhanced.

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Point-by-point response to referee's comments and suggestions

Ultralow CNT-Reinforced Phase-Change Fibers for Scalable Wearable Thermoregulation

We sincerely thank the editor and reviewers for their valuable comments and suggestions, which have resulted in modifications that have improved the quality and clarity of our manuscript. To address the specific points clearly, we have separated the reviewer's comments into questions and answered them as follows:

Reviewer #1

This manuscript introduces a nanotechnology-inspired strategy that combines ultralow CNT (0.1 wt.%) heterostructures with gradient crystallinity engineering to produce scalable PCFs, and these fibers exhibit exceptional synergy between thermal storage density and adaptive thermal regulation capabilities. The integrated experimental and MD studies elucidate three synergistic strategies to optimize PCFs performance: 3D-IPNs confinement engineering, CNT-induced structural modulation, and a scalable manufacturing paradigm. Furthermore, these fibers can be cut and sewing to PCM-based thermoregulatory clothing that outperforms traditional polyester fabrics in thermal regulation, maintaining stable thermal conditions under dynamic environmental temperatures, while demonstrating transformative potential for wearable systems in extreme-environment applications and medical thermotherapy applications. Overall, the methodology is reasonable and logical. Below are a few comments on your manuscript.

Our response: Thank you very much for your positive comments and constructive suggestion.

1. In this manuscript, authors obtained C22/CNT fibers from primary fibers that underwent 3 stretching cycles, so how to balance the relationship between the number of stretching cycles and mechanical properties of fibers? Will increasing the number of stretching cycles further enhance the final mechanical properties of the fibers?

Our response: Thank you very much for your invaluable suggestion. To further investigate the relationship between the stretching numbers and mechanical properties, we conducted additional a series of controlled experiments to isolate each processing stage and characterize its stage-specific mechanical property.

The experimental results demonstrate that the mechanical properties of fibers such as elastic modulus, toughness, and strength gradually enhanced with the increase of stretching cyclic stimulation (Fig. R1a, b and c). We found that the mechanical properties of the fibers (e.g., tensile strength and modulus) increase significantly during the first 3 cycles. Upon attempting a fourth stretching cycles, the fiber's fracture toughness decreased markedly, rendering it excessively brittle and making continuous collection difficult. The significant reduction in fracture strain after the fourth drawing cycle further suggests the possible accumulation of internal damage within the fiber (Fig. R1c). Thus, there is a balance between the number of stretching cycles and the mechanical properties. The initial stretching efficiently enhances fiber orientation and density, but subsequent steps yield diminishing returns while progressively accumulating irreversible damage (e.g., interface slippage and defect propagation). The selection of three stretching cycles represents an optimal balance, maximizing structural improvement before the onset of significant damage.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 7, Lines 189-194) and **Supporting Information** (Page 12, Lines 296, Page 13, Lines 297-318, Page 28, Fig. S14).

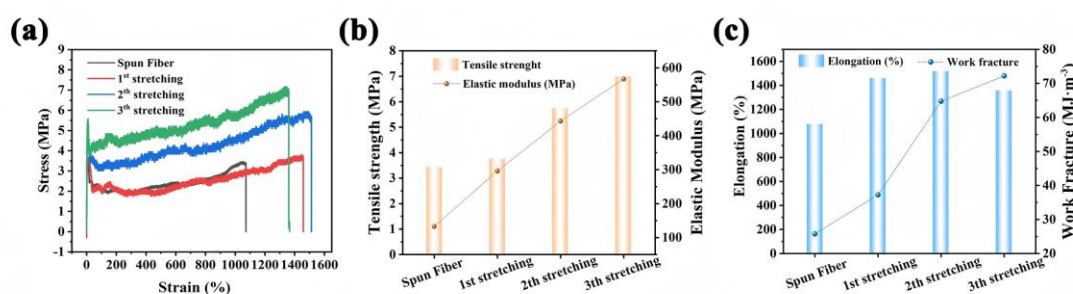


Fig. R1 (a) Stress-strain curves, (b) Comparison of the tensile strength and elastic

modulus, (c) Comparison of the elongation at break and toughness of C22/CNT2 Fiber with different stretching cycle.

2. On line 207 of page 9, “single-roll C22/CNT3 fibers (with a diameter of 200 nm and inner width of 56 nm)”, the diameter should be length.

Our response: Thank you very much for pointing it out. I do apologize this mistake, and revised it accordingly (Page 9, Lines 221-222, Page 9, Lines 235).

3. On line 335 of page 13, “Free energy analysis revealed that CNT-induce nucleation barrier reductions in nucleation barriers were attributed to decreases in interfacial energy and strain energy minimization”, could the author further visually demonstrate how the interfacial energy and strain energy changes?

Our response: We do appreciate the invaluable and insightful comments. Visualizing the evolution of interfacial energy and strain energy would provide compelling evidence for our conclusion that CNTs effectively reduce the nucleation barrier. To further investigate the evolution of interfacial and strain energy during crystallization, we have included the following supplementary analysis and discussion:

The interfacial interaction energy (E_{inter}) was evaluated using the formula:

$$E_{inter} = E_{total} - (E_{CNT} + E_{C22}) \quad (1)$$

Where E_{total} is the energy of the composite system, and E_{CNT} and E_{C22} are the energies of the separate components.

The system with low CNT loading achieves a markedly lower interfacial energy during crystallization, as evidenced by its rapid decrease in Fig. R2a. This suggests that a small amount of CNT provides a low-energy interface for n-docosane. At this moment, the nucleation barrier for heterogeneous crystallization, which is governed by the interfacial energy term, becomes significantly lower than that for homogeneous nucleation according to the heterogeneous nucleation theory. The synergistic decline in both E_{angle} and $E_{torsion}$ (Fig. R2b) indicates that the molecular segments integrate into the crystal lattice with minimal conformational adjustment. MD snapshots visually

confirm this phenomenon: in the low-CNT loading system, n-docosane molecules adsorbed on the CNT surface undergo only subtle conformational adjustment (Fig. R3a₁a₂, b₁b₂). A small lattice mismatch exists between the CNT and the crystal, thereby suppressing lattice distortion during the growth of the nucleus and facilitating the formation of a low-strain nucleus. This strain energy relief facilitates a rapid nucleation rate by lowering the energy barrier for stable nucleus formation. In contrast, the system with excessive CNT loading induces significant conformational rearrangement of n-docosane at the interface due to stronger interfacial interactions (Fig. R3c₁c₂). Thus, a small amount of CNTs functions as heterogeneous nucleating agents by progressively lowering the interfacial energy and inducing a pre-ordered structure (which reduces strain energy), thereby mitigating molecular-level energy barriers.

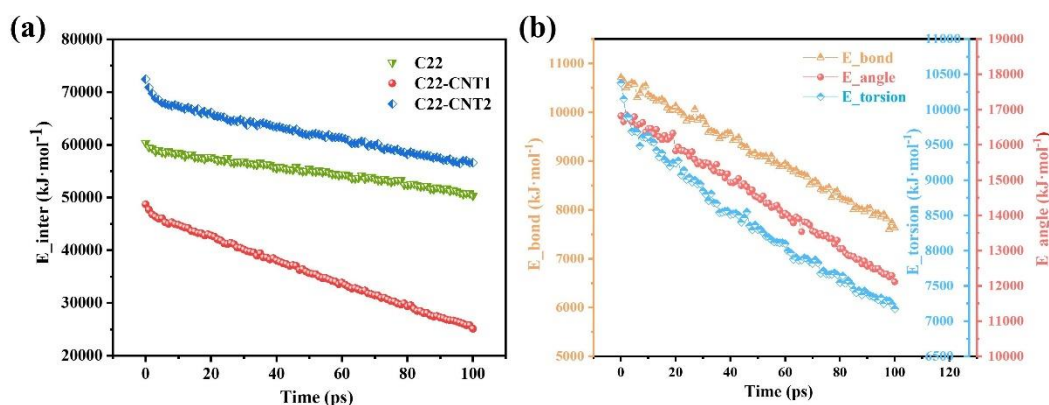


Fig. R2 (a) Variations in interfacial interaction energy of the phase-change composite system over time during the cooling process, (b) Variations in bond energy, angle energy and torsion energy of C22/CNT1 system during the cooling process.

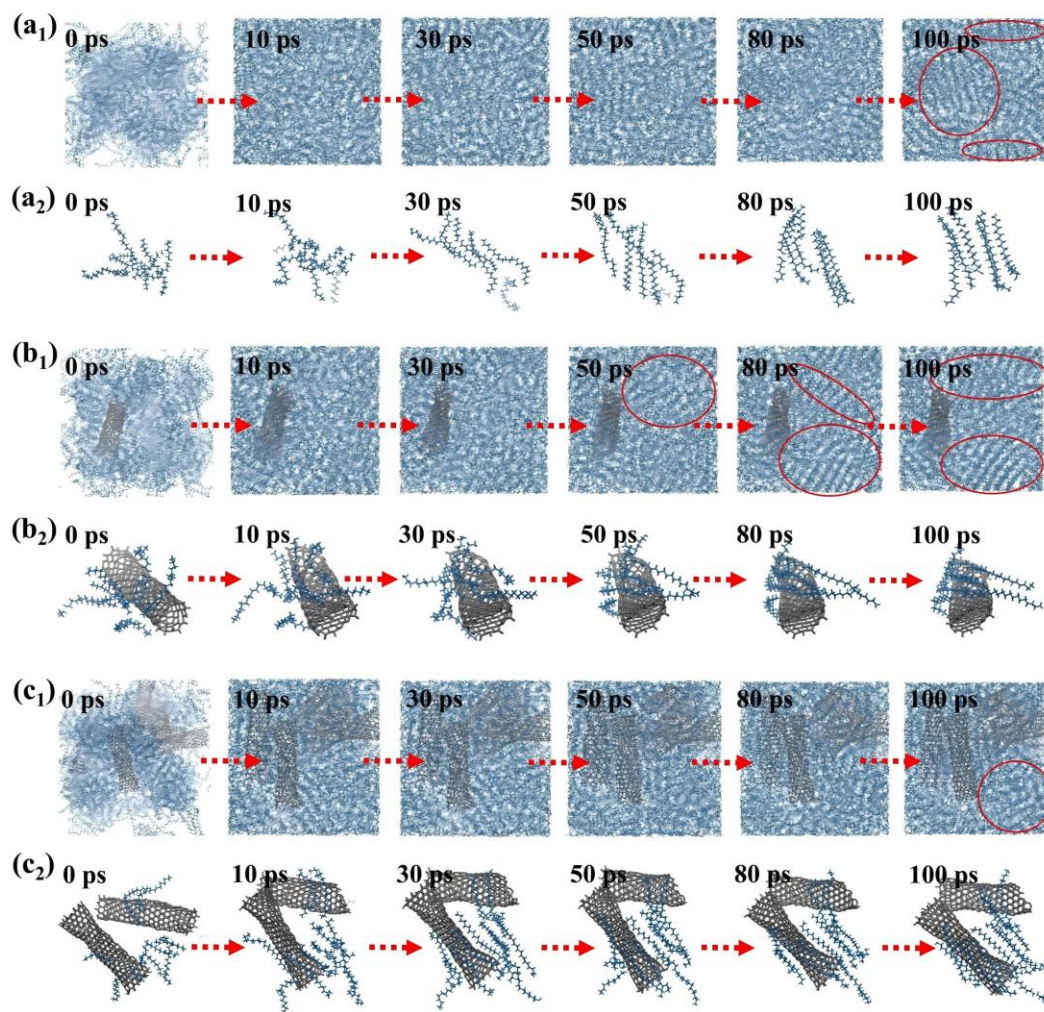


Fig. R3 MD snapshots (local zoom) of the crystallization process of: (a) n-docosane, (b) n-docosane with one CNT (denoted as C22/CNT1, 0.1 wt.%), and (c) n-docosane with six CNTs (denoted as C22/CNT2, > 0.5 wt.%) at 0 ps, 10 ps, 30 ps, 50ps, 80 ps, and 100ps.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 14, Lines 365 and 368-377, Page 15, Lines 378-389) and **References** (Page 38, Lines 1029), and **Supporting Information** (Page 18, Lines 446-453, Page 21, Lines 527-538, Page 43, Fig.S31, Page 44, Fig. S32).

4. Please check the reference citation format in the manuscript, for example, line 355

of page 15.

Our response: Thank you very much for pointing it out. We do apologize for these mistakes. We have carefully checked and standardized the reference citation formatting throughout the entire manuscript. Specifically, for the example mentioned (Line 355 of Page 15), we have corrected them to conform the required citation style. These revisions are highlighted in blue. Please kindly refer to **the Results** (Page 16, Lines 410-411, Page 27, Lines 671)

5. Part of the description in Fig.4 shows unclear font display. Additionally, what stage is the RDF distribution in Fig. 4i?

Our response: We appreciate the reviewer's invaluable comments. The RDF is used to characterize the evolution of the polymer-CNT interface during tensile deformation, which tracks the density profile of polymer carbon atoms relative to the CNT axis. The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 24, Lines 612-617 and 619-621, Page 27, Lines 667-668), and **Supporting Information** (Page 22, Lines 574-582, Page 23, Lines 584-586).

6. What of the set stress strain rate in MD simulation? Is there any experimental verification?

Our response: Thank you for the reviewer's invaluable comments. In our MD simulation, a strain rate of $2 \times 10^{12} \text{ s}^{-1}$ was employed, which is different with the constant strain rate of $8.35 \times 10^{-3} \text{ s}^{-1}$ in the tensile experiment. In most similar MD simulations, the employed strain rates are typically on the order of $10^8 \text{ s}^{-1} \sim 10^{12} \text{ s}^{-1}$, which are many orders of magnitude higher than those in conventional mechanical tests (typically $10^{-3} \text{ s}^{-1} \sim 10^0 \text{ s}^{-1}$). This is dictated by the inherent limitations of the computational time scale. Because such high loading rates are essential to accelerate the dynamics and observe a complete deformation or failure event within the practically accessible simulation timeframe of nanoseconds to microseconds. Furthermore, numerous studies have

confirmed that the choice of strain rate in MD simulations does not alter the fundamental characteristics or qualitative trends of the stress-strain response in composite materials under identical simulation conditions of temperature and pressure. Under the stress-strain rate of $2 \times 10^{12} \text{ s}^{-1}$, our simulations successfully predict that a low-CNT loading significantly enhances key macroscopic mechanical properties, including fracture strain, modulus, and toughness. This trend aligns qualitatively with our experimental tensile tests, as shown in Fig. 5a and b. Importantly, the simulations provide an atomistic-scale explanation for this macroscopic phenomenon: CNTs act as effective alignment templates and reinforcing agents, enhancing the mechanical properties of the composite fibers.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Supporting Information** (Page 12, Lines 269-276).

7. In the supporting documents, I think that the introduction to the subsections in section 1.6 is redundant. Additionally, relevant references and reasons should be provided for the rationality of the selection of the force field.

Our response: We appreciate the reviewer's invaluable comments. As suggested, we have streamlined Section 1.6 by removing the redundant introductory text. Moreover, we appreciate you raising this critical point regarding force field selection. We fully agree that the choice of force field serves as the foundation for ensuring the reliability of molecular dynamics simulation results. We have provided the relevant references and reasons for the rationality of the selection of the force field, and these revisions are highlighted in blue. Please kindly refer to **the Supporting Information** (Page 6, Lines 138-158, Page 7, Lines 164, Page 7, Lines 169-172, and Page 7, Lines 175), and **References** (Page 65, Lines 1038-1070).

Reviewer #2

The manuscript reports phase-change fibers by incorporating ultralow CNT loadings into an interpenetrating polymer network (HDPE/SEBS). The authors demonstrate high latent heat storage, enhanced mechanical robustness, and improved thermal conductivity in the fiber. The work is interesting, combining experiments and molecular dynamics simulations, and demonstrates potential applications in wearable thermal management. However, there are several concerns that should be addressed before the manuscript can be considered for publication.

Our Response: We are grateful for the positive comments and constructive suggestion. We have carefully revised our manuscript according to these invaluable suggestions and comments.

1. In Fig.2c, the authors assign the observed lattice spacing of 0.32 nm to the HDPE. Could the authors clarify which crystallographic plane of it corresponds to? The reported d spacing is 0.32 nm, but the (110) and (200) plane of orthorhombic PE have strong diffraction at d-spacing of around 0.41 nm and 0.37 nm, respectively (e.g., Polymer, 2021, 212: 123164). Is it possible to be something else?

Our response: We appreciate the reviewer's crucial comments. We do apologize for this oversight and have corrected it with a detailed explanation in the revised manuscript. The spacing of 0.32 nm that we observed does not match any major diffraction plane of HDPE. Following a careful re-examination and analysis, we provide the following interpretation and correction for this result:

The observed d-spacing of 0.32 nm is a characteristic signature corresponding to the (002) lattice plane of graphitic carbon materials. In our composite system, this spacing corresponding unambiguously to the inter-wall distance between the graphitic layers of the carbon nanotube. Therefore, the lattice fringes measuring 0.32 nm in Fig. R2c should be accurately attributed to the intrinsic lattice structure of the CNT, rather than to a crystalline phase of HDPE. This provides strong evidence that the CNTs maintain their structural integrity within the composite. Re-examination of the HRTEM image confirms that the fringe-containing region displays distinct phase contrast and

morphology from the surrounding polymer, presenting characteristic features of carbon nanotubes.

Despite the CNT features shown in this image, the X-ray diffraction (XRD) pattern of the composite materials still reveals diffraction peaks at approximately 0.41 nm and 0.37 nm, which confirms the presence of the HDPE crystalline phase. Furthermore, to further verify the crystalline structure of HDPE, we re-examined the fiber using HRTEM and performed FFT analysis via GMS3 software on HRTEM images of the polymer matrix regions. The LiveFFT diffraction pattern clearly revealed two distinct diffraction spots corresponding to lattice spacing of 0.41 nm and 0.37 nm (see Fig. R4ab), with measured interplanar distance of 0.413 nm (see Fig. R4c). These values show excellent agreement with the (110) and (200) planes of orthorhombic polyethylene, respectively, as established in literature (e.g., Polymer, 2021, 212: 123164). This confirms unequivocally that the observed lattice fringes in this region originate from the crystalline phase of HDPE rather than other components.

The original description did not sufficiently highlight this analytical process. We have therefore revised the manuscript to explicitly state in the main text that this conclusion is grounded in precise measurements of the FFT diffraction pattern.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 10, Lines 257-258 and 260-268, Page 11, Fig. 2), **References** (Page 38, Lines 1026-1027), and **Supporting Information** (Page 12, Lines 291-295, Page 27, Fig. S13).

We are grateful for your insightful review. This correction has significantly enhanced the accuracy and scientific rigor of our work.

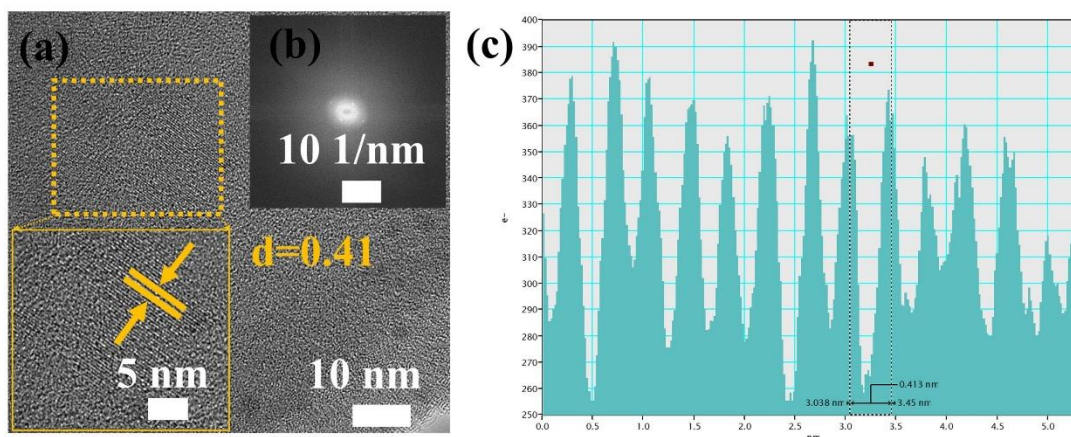


Fig. R4 (a), (b) and (c) Lattice fringe of HDPE inside C22/CNT2 fiber

2. The MD simulations in Fig.3 focus in the interaction between n-docosane and CNTs, which demonstrates the heterogeneous nucleation and crystallization behavior. However, the actual fiber system also contains HDPE and SEBS, which may significantly influence molecular confinement and crystallization dynamics. Could the authors explain why these polymer components were not included in the simulations, and discuss whether this might limit the accuracy or completeness of the MD interpretation?

Our response: We do appreciate the reviewer's invaluable comments. We completely agree that HDPE and SEBS would contribute additional complexity to the crystallization kinetics and confinement effects in the practical system.

The primary objective of this MD study is to directly verify and visualize the core physical mechanism of CNT-induced heterogeneous nucleation in n-docosane (C22) at the molecular level. The simulation dissects the effect of CNT loadings on the heterogeneous nucleation of n-docosane. By excluding interactions from HDPE and SEBS, this simplified approach enables us to isolate and directly probe the fundamental interfacial interactions between CNT and C22, revealing the effect of low CNT loading on induced crystallization.

We thank you for your insightful comment regarding the inclusion of HDPE and SEBS in our simulations. Considering the realistic sample situation, we constructed three comprehensive full-component systems models including SEBS-HDPE-C22, SEBS-

HDPE-C22-3CNT (0.1 wt% CNT loading), SEBS-HDPE-C22-18CNT (> 0.5 wt.% loading) for simulation. These additional simulations not only directly address your concern but also greatly enhanced our understanding of crystallization behavior in the multicomponent composite system.

Specifically, to perform the crystallization simulation in a realistic environment, the size of boxes for the three systems simulated above (0CNT, 3CNT, 18CNT) is increased to $15.0\text{ nm} \times 15.0\text{ nm} \times 15.0\text{ nm}$ (see Figs. R5-7). In the production run, a time step of 1 fs was used, and the data were collected every 1 ps. The energy and force of the system were optimized (including atomic positions and box sizes). All production runs were under in microcanonical ensemble at 298 K and 1 bar pressure for 10 ps to equilibration. Then the cooling NVT ensemble was carried out from 353 K to 293 K to obtain the parameters of the system at the end of the simulations. Periodic boundary conditions were applied in all directions.



Fig. R5 Structure of SEBS model

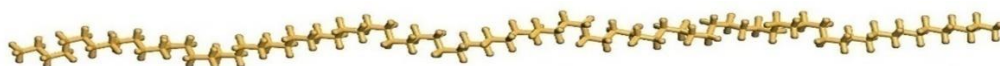


Fig. R6 Structure of HDPE model

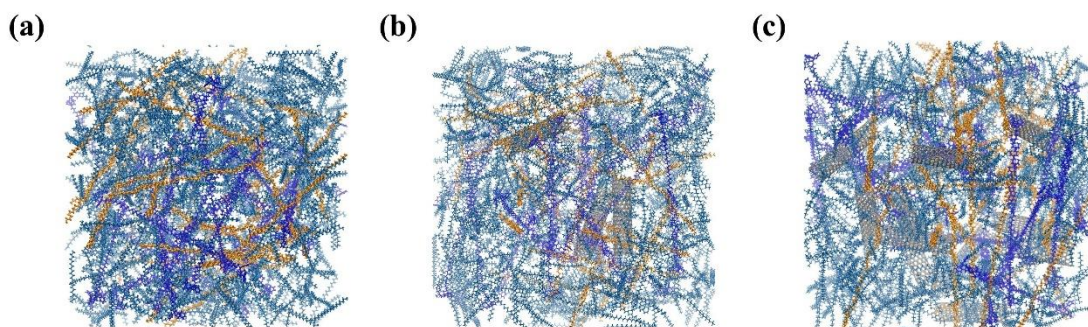


Fig. R7 The comprehensive full-component system (SEBS-HDPE-C22-CNT) model

with (a) 0 CNT, (b) 3 CNT (0.1 wt.%), and (c) 18 CNTs (> 0.5 wt.%).

Across all three full-component systems, MD snapshots showed no emergence of ordered n-docosane arrangements during crystallization (see Fig. R8), confirming that SEBS and HDPE spatially confine n-docosane as you anticipated. Furthermore, while serving as a structural scaffold, these polymers effectively prevent n-docosane leakage – behavior fully consistent with the morphological stability observed in our experiments. Despite this confinement, we clearly observed that in the presence of CNTs, both the molecular chains of polymer and n-docosane are co-adsorbed onto the CNT surface (see Fig. R8b₁b₂c₁c₂). Initially characterized by a disordered atomic arrangement, the interface of molecular chain and CNT exhibits high interfacial energy and considerable local strain (see Fig. R9). As crystallization proceeds, crystalline nucleus emerges on the CNT surface, displaying a well-defined epitaxial match with the CNT lattice in the low-CNT loading systems, which is different from the initial state. This indicates that molecular chains are rapidly adsorbed onto the CNT surface with only subtle conformational adjustment, forming a pre-oriented layer in the low-CNT loading system (see Fig. R8b₁b₂). In contrast, the system with excessive CNT loading induces significant conformational rearrangement of molecular chains at the interface due to strong interfacial interactions (see Fig. R8c₁c₂). This finding demonstrates that a small amount of CNTs remain potent heterogeneous nucleating agents even within complex multicomponent environments, thereby validating the universality and reliability of the core mechanism identified by our initial model.

Compared to the initial model, analysis of the mean squared displacement (MSD) curves for different components across the three full-component systems reveals that although n-docosane, HDPE, SEBS exhibit relatively high initial diffusion rates, their overall dynamics are ultimately compromised used to constraints imposed by the cross-linking network of polymer molecular chains (see Fig. R10). Furthermore, in higher CNT loading system, the formation of percolating network restricted molecular mobility, leading to a reduction in overall crystallinity. In contrast, in low-CNT loading

system, the diffusion rates of SEBS and HDPE remained comparable to those in the pure C22 system, while the MSD curves of n-docosane molecules indicated rapid condensation (crystallization) induced by CNTs. This kinetically confirms that a low CNT concentration can efficiently guide the ordering of n-docosane molecules.

Furthermore, we performed a comprehensive analysis of the total potential energy, bond energy, non-bonded interaction energy, and interfacial interaction energy of three full-component systems during the crystallization process (see Fig. R9). The results demonstrated that the system with low-CNT loading exhibits the most rapid decrease in energy (including E_{total} , E_{bond} , E_{angle} , E_{torsion} , E_{inter}) and achieves the lowest final energy state, indicating the most stable configuration (see Fig. R9). This provides compelling thermodynamic evidence that this system forms a more stable crystalline structure, unequivocally highlighting the significant advantage of a small amount of CNT as a heterogeneous nucleating agent in reducing the nucleation barrier and promoting overall system stability.

These MD simulation results of comprehensive full-component models are fully consistent with the conclusions from our initial simplified model. The simplified model successfully isolated and revealed the heterogeneous nucleation mechanism induced by a small amount of CNT, while the full-component model validates the effectiveness of this mechanism under realistic conditions, while additionally revealing the confinement effects imposed by the polymer components.

Thank you again for your invaluable comments. We have added a dedicated section in the revised manuscript to present these results of full-component system simulation and corresponding discussions in detail.

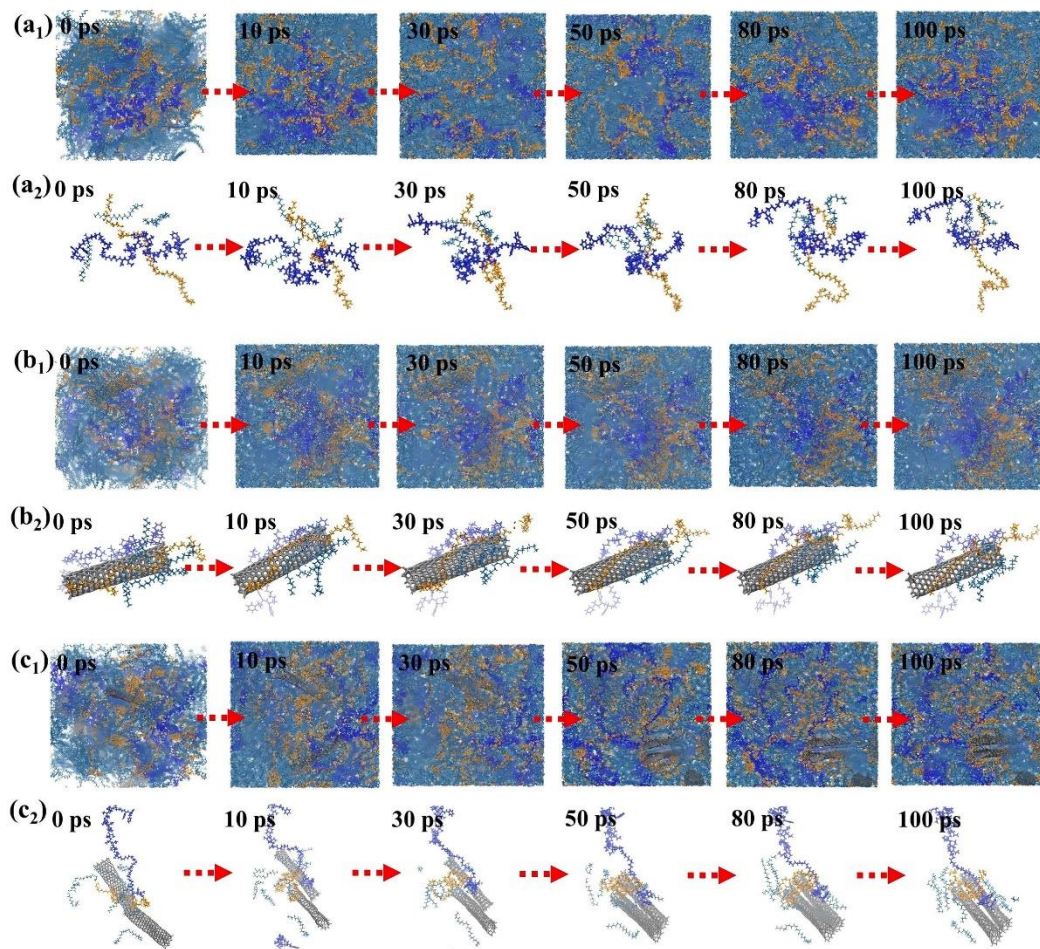


Fig. R8 MD snapshots and corresponding local area of the crystallization process of: (a) C22@SEBS-HDPE, (b) C22/CNT1@SEBS-HDPE (0.1 wt.% CNT loading), and C22/CNT2@SEBS-HDPE (> 0.5 wt.% CNT loading) at 0 ps, 10 ps, 30 ps, 50 ps, and 100 ps, respectively.

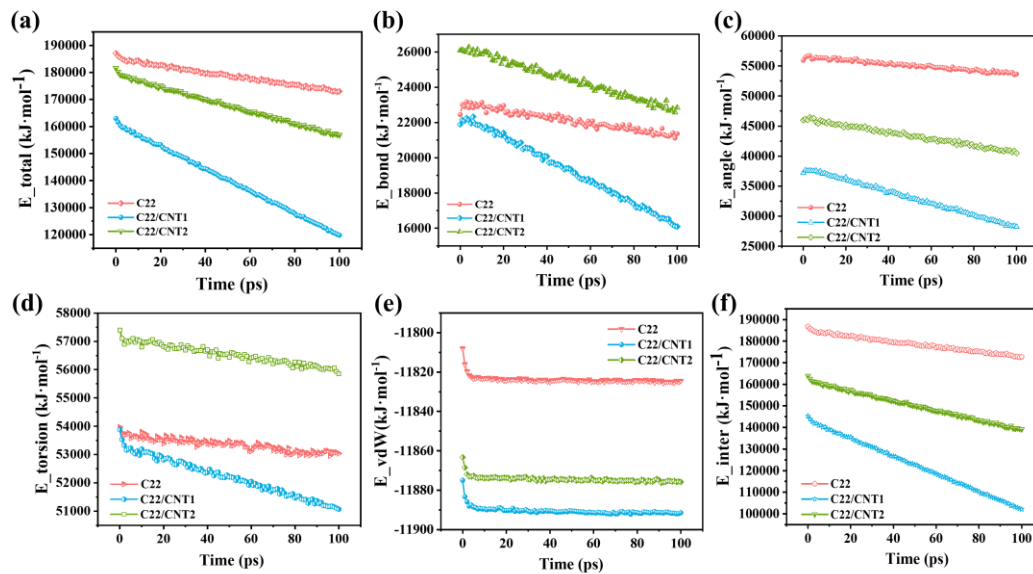


Fig. R9 Variations in potential energy (a), bond energy (b), angle energy (c), torsion energy (d), van der Waals energy (e), interfacial interaction energy (f) of n-docosane, C22/CNT1 system, C22/CNT2 system following the extension of time during the crystallization process.

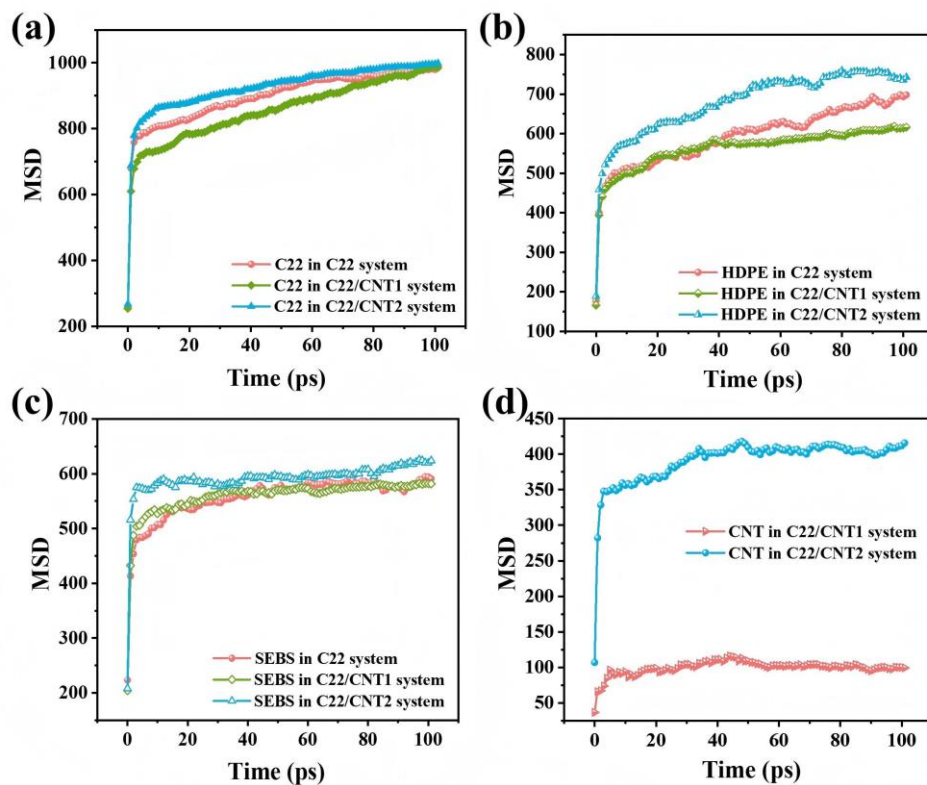


Fig. R10 Mean square displacement of C22 (a), HDPE (b), SEBS (c), and CNT (d) within C22 system, C22/CNT1 system, and C22/CNT2 system, respectively.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 17, Lines 418-445, Page 18, Lines 446-470, Page 19, Lines 473-482, and Fig. 4), and **Supporting Information** (Page 8, Fig. S4 and Fig. S5, Page 10, Lines 229-237, and Fig. S7, Page 45, Fig. S33 and S34).

3. The manuscript claims that the melt-spinning and multi-stage stretching processes largely influence chain orientation and crystallization behavior of the fibers. However, the DSC analysis only compares fibers with different CNT loadings, without showing the thermal response of the unspun precursor and the fibers without stretching. Including a comparison of enthalpy before and after spinning and stretching would strengthen the mechanistic interpretation.

Our response: We do appreciate the reviewer's invaluable comments. Your feedback is crucially important for developing a more robust argument and a deeper mechanistic understanding. We designed and conducted a series of controlled experiments to isolate each processing stage and characterize its stage-specific crystallization behavior.

We prepared five key control samples to delineate the structural evolution throughout the processing stages:

- (1) Composite phase change masterbatch (Unprocessed precursor):

The raw material that has not undergone any spinning or stretching treatment.

- (2) As-spun fiber (primary fiber):

Fiber that has only undergone melt spinning without any subsequent stretching.

- (3) Single stretching fiber (1st stretching fiber):

Fiber that has completed the melt-spinning process and has undergone a single stretching step.

- (4) Twice stretching fiber (2th stretching fiber):

Fiber that has undergone complete melt spinning followed by two sequential stretching processes.

(5) Triple stretching fiber (3th stretching fiber):

The ultimate fiber produced through the complete process route, including both melt-spinning and the full multi-stage stretching processes.

We performed detailed differential scanning calorimetry (DSC) analysis on these five samples and have incorporated the corresponding DSC thermograms, enthalpies of melting and crystallization, and their interpretation (see the relevant figure) into the revised manuscript.

The DSC analysis tracing the structural evolution from the composite phase-change masterbatch to the as-spun fiber and finally to the full-process fiber reveals a clear trend: both melting and crystallization peaks show successive sharpening, while the crystallization peak temperature shifts markedly toward higher temperatures (Fig. R11a). These changes indicate a progressive enhancement in crystal perfection and crystal size with each processing step. Moreover, the stepwise increase in enthalpy provides decisive quantitative evidence for the proposed process-structure relationship (see Fig. R11b and Table R1). This result reveals that melt spinning, with its rapid shear and quenching conditions, induces preliminary molecular orientation and limited crystallization. However, the multi-stage stretching process is the most critical step for achieving a high degree of crystallinity. Two characteristic peaks of C22/CNT fibers at $2\theta = 21.3^\circ$ and 23.2° in the XRD pattern (Fig. R12a) correspond to the (110) and (200) crystal planes of orthorhombic polyethylene. The characteristic peaks of C22/CNT fiber at $2\theta = 19.2^\circ$, 19.6° , 22.3° , 23.3° , 24.7° and 25.6° belong to n-docosane. The XRD results indicate that the diffraction intensity systematically increases with successive stretching steps, providing direct evidence of the structural evolution (see Fig. R12b). This demonstrates that the multi-stage stretching process is the dominant factor in achieving high molecular orientation, with an effect that substantially exceeds the preliminary alignment achieved by melt-spinning alone. This strongly demonstrates the dominant role of the stretching process in promoting further chain orientation, slip, and

rearrangement, thereby facilitating the formation of a more perfected and stable crystalline structure.

Furthermore, we conducted mechanical tests on the samples to further investigate the effect of stretching-induced molecular chain orientation and crystallization on the mechanical properties of the fibers (see Fig. R13). The results for single-fiber mechanical testing are fully consistent with the structural evolution detailed above. Compared to the as-spun fibers, the multi-stage stretching fibers exhibit remarkable increases in tensile strength and modulus of approximately 106.5% and 331.8%, respectively. This mechanical enhancement correlates directly with the improved molecular orientation revealed by XRD and the increased crystallinity indicated by DSC. These results collectively demonstrate that multi-stage stretching process promotes chain alignment and crystal perfection, thereby substantially enhancing mechanical performance.

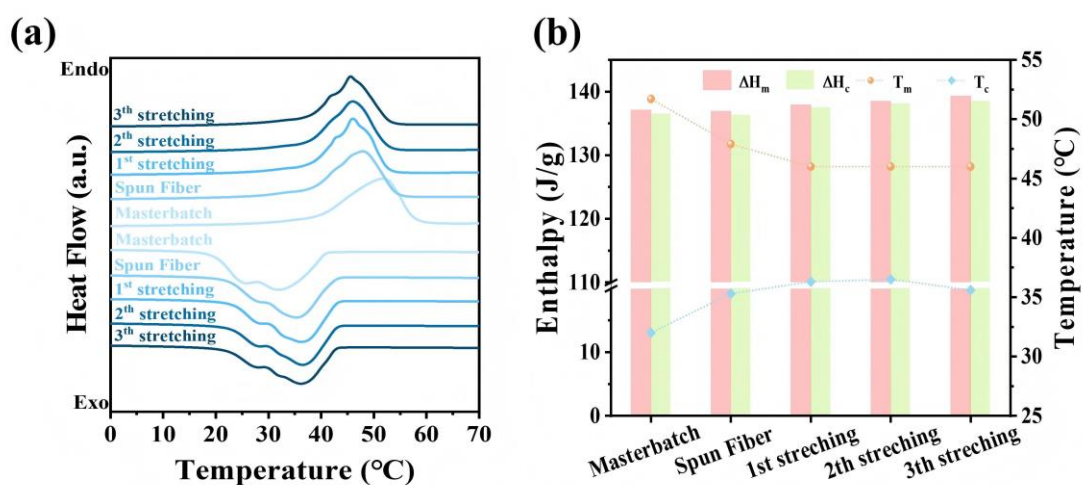


Fig. R11 (a) DSC curves, and (b) Enthalpy and phase-change temperature of C22/CNT2 fibers under different stretching cycle

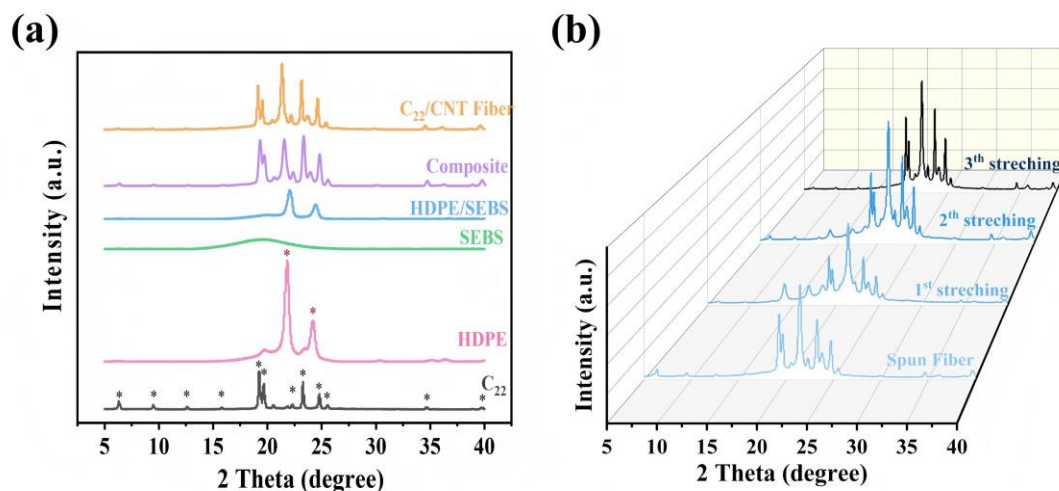


Fig. R12 Powder X-ray diffraction (XRD) of (a) C22, HDPE, SEBS, HDPE/SEBS, C22/CNT@HDPE-SEBS, C22/CNT2 fiber, and (b) C22/CNT2 fiber under different stretching cycles

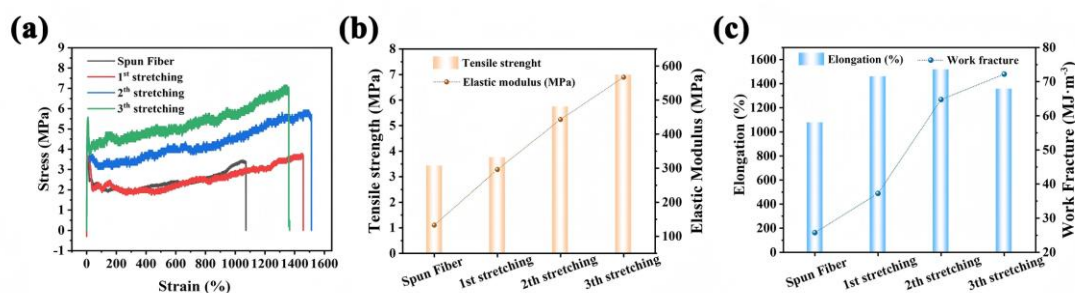


Fig. R13 (a) Stress-strain curves, (b) Comparison of the tensile strength and elastic modulus, and (c) Comparison of the elongation at break and toughness of C22/CNT2 fibers under different stretching cycles

Table R1 Thermal properties of C22/CNT2 fibers under different stretching cycle

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
Masterbatch	51.7	137.1	32	136.5
Spun Fiber	47.9	136.9	35.3	136.3
1 st stretching fiber	46	137.9	36.3	137.5
2 th stretching fiber	46	138.5	36.5	138.1
3 th stretching fiber	46	139.3	35.6	138.5

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 6, Lines 170-174, Page 7, Lines 175-194,) and **Supporting Information** (Page 12, Lines 279-296, Page 13, Lines 297-318, Page 26, Fig. S12, Page 27, Fig. S13, Page 28, Fig. S14, Page 61, Table S1).

We sincerely thank you for this profound and constructive guidance. The controlled experiments you recommended were instrumental in bridging the logical gaps in our original argument and establishing a complete evidentiary chain for the proposed mechanism. Your input has significantly enhanced the scientific rigor and impact on our study.

4. While the manuscript claims 0.1 wt.% CNT as the optimal loading for performance (thermal stability, latent heat, and mechanical strength), the orientation degree (Fig.4d) and elongation at break (Fig.4b) are highest with 0.05 wt.% CNT. It would be helpful if the authors could further discuss why the optimal CNT content differs depending on the performance metric.

Our response: We do appreciate the reviewer's thoughtful and constructive comments. The ideal loading is a relative concept, intrinsically dependent on the targeted property. This observed variation is fundamentally a manifestation of the competition between performance metrics in a multi-objective design space, where each property is governed by a distinct microstructural evolution pathway and reinforcement mechanism.

Under lower CNT loading conditions (0.05 wt.%), CNTs are primarily individually dispersed, which facilitates their uniform distribution within the polymer matrix and allows them to be sufficiently wetted by the polymer. Thus, these individually dispersed CNTs can more readily align along the direction of shear or tensile flow during melt processing. The stretching process further facilitates the alignment of these well-dispersed, low-content CNTs along the stretch direction, yielding a high degree of orientation. This high orientation, combined with good dispersion, is pivotal for efficient stress transfer.

When the CNT content increases to 0.1 wt.%, the intensified van der Waals interactions between CNTs promote the formation of local aggregates. This promotes the formation of a robust percolating network, acts as enhanced physical cross-links and thermal barriers within the composites, contributing to enhancing thermal stability and mechanical strength (e.g., higher tensile strength and modulus). Furthermore, the denser CNT network provides a sufficient number of uniform nucleation sites, promoting more perfect overall crystallization. As suggested by Valentini ¹, the heterogeneous nucleation efficiency of CNTs does not increase linearly with their content but rather exhibits a saturation behavior. An insufficient amount (e.g., 0.05 wt.%) offers too few sites to maximize this effect, while an excessive amount may hinder crystal perfection due to spatial confinement. Thus, although some local aggregation occurs, slightly reducing local orientation degree, the network effect outweighs the detriment, delivering the best balance of strength, thermal properties and latent heat.

In short, the 0.05 wt.% CNT loading represents the microstructural threshold for optimal dispersion, maximizing the “single-fiber toughening effect”, whereas 0.1 wt.% activates the “three-dimensional network enhancement effect”, optimizing the trade-off between strength, thermal stability, and latent heat.

For our target application – phase change fibers requiring reliable thermal performance, energy density, and load-bearing capacity – the 0.1 wt.% CNT loading was selected as the system-wide optimum. This choice reflects a design strategy that prioritizes multifunctional performance over a single metric.

The relevant expressions have been carefully revised and necessary explanations have been added to the manuscript, and these revisions are highlighted in blue. Please kindly refer to **the Results** (Page 21, Lines 540-546, Page 22, Lines 547-567) and **References** (Page 41, Lines 1157-1159).

Reference

1. Valentini L, Biagiotti J, Kenny JM, Santucci S. Effects of single-walled carbon nanotubes on the crystallization behavior of polypropylene. Journal of Applied

Polymer Science, 2003, 4, 708-713.

5. There are some typos and grammatical error (e.g., “blew 40%” should be “below 40%”). In addition, the fonts in some figures are too small (e.g. Fig. 4a-d, etc.)

Our response: We apologize these mistakes. We have checked the whole manuscript, and corrected these mistakes accordingly.

Point-by-point response to referee's comments and suggestions

Ultralow CNT-Reinforced Phase-Change Fibers for Scalable Wearable Thermoregulation

We sincerely thank the editor and reviewers for their valuable and positive comments.

Reviewer #1

I have carefully read the authors' responses and the revised manuscript. In my view, the main concerns raised in my previous report have been adequately addressed, and the presentation has been significantly improved. I therefore consider the manuscript suitable for publication in this present form.

Our response: Thank you very much for your positive comments.

Reviewer #2

My concerns were addressed, and the manuscript quality is enhanced.

Our response: Thank you very much for your positive comments.