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Impact of torsion and stretching on the thermal conductivity of polyethylene strands

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A single polyethylene chain was reported to have a high metal-like thermal conductivity (TC), which stands in sharp contrast to the thermally insulating feature of common bulk polyethylene materials. This work numerically investigates the impact of torsion and stretching on the TC of polyethylene strands by using equilibrium molecular dynamics simulations. The simulation results show that torsion slightly reduces the TC of a single polyethylene chain. In contrast, the heat conduction of polyethylene strands could be slightly enhanced under torsional loading with a specific torsional angle. Particularly, an apparent improvement of TC of polyethylene strands is achieved by combining torsion and stretching functions. It is found that the TC of torsional polyethylene strands is sensitive to torsional patterns. Our study proposes a specific torsional pattern of polyethylene strands that significantly enhances the heat conduction of the original counterpart. This study will play an essential role in guiding the improvements of thermal conduction property of polymers.

Polymers have been applied in a wide variety of engineering applications due to their outstanding physical properties, including high toughness, strong corrosion resistance, low density, and low cost. As one important transport property, thermal conductivity (TC) of polymers largely depends on the macromolecule configuration. The low TC of bulk polymers, on the order of 0.1–1 W/(m·K), significantly limits their applications in thermal engineering fields.1–3 Previous studies showed that a single polyethylene (PE) chain and well-aligned PE chains can have substantially improved TC. For example, Henry and Chen observed through molecular dynamics (MD) simulations that the ultimate TC of a suspended PE chain could reach ~350 W/(m·K) at room temperature.4,5 Their subsequent experimental work convincingly verified that the ultra-drawn PE nanofibers possess a TC as high as 104 W/(m·K).6 Cao’s group fabricated PE nanowire arrays via an improved nanoporous template wetting technique, resulting in a TC of approximately 6–10 W/(m·K), about two orders of magnitude higher than those of the bulk polyethylene materials.7 Hu et al. confirmed the high TC of a single PE chain by using equilibrium molecular dynamics (EMD) simulations.8 Lin et al. also reported that the TC of a stretched PE chain increased with increasing strains, based on their numerical simulation results.9 All of the above studies confirmed the high TC of oriented PE chains. Recently, Liao et al. proposed the aligned carbon nanotube–polyethylene composites that achieved TC almost twice as high as that of a single PE chain.10 Doping the disordered insulating polymer matrix with thermally conductive additives such as carbon nanotubes (CNTs) or graphene is a common practice. However, the overall TC remains relatively low because the heat transport is strongly limited by the interfaces in the composite.11,12 Additionally, doping may be harmful to the outstanding mechanical properties of polymers.

It was shown that increasing the orientation order of polymer chains is an effective approach to enhance the TC of amorphous polymer materials.6–8 Generally, stretching, shear, and torsion are three major physical functions to influence molecular structures. Little work has been done to improve the heat transfer mechanism of polymer chains under these physical conditions. Previous studies found that the torsional effect was the main cause of the ultra-low TC of bulk polymers.13–15 However, Rob Janssen’s group measured the TC of molecularly aligned ultrahigh molecular weight polyethylene ropes to be 45 W/(m·K), even higher than that of oriented PE chain arrays.16 The key question is whether the torsional effect is advantageous to the formation of crystal structure. Therefore, it is meaningful to systematically investigate the intrinsic TC of various PE strands under torsional and stretching conditions. Our study will help to gain fundamental insight into the improvements of the TC of polymers.

The classical equilibrium molecular dynamics method was adopted to explore the TC of PE structures,17–25 including suspended PE chains, torsional PE chains, PE strands consisting of several PE chains, and torsional PE strands at room temperature. The MD simulation details are available in the supplementary material. Figure 1 shows the representative structures of original PE chains, a single torsional PE chain, and torsional PE strands, respectively. The lengths of

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torsional structures are consistent with the length of non-torsional ones during the modeling process. In the torsion modeling, we secured one end of the chains, twisted each segment, and finally relaxed the torsional chains. All torsional strands were obtained in the same way. The periodic boundary condition maintains the torsion during simulation by linking each chain end-to-end. The torsion and stretching are apparently maintained when the structures are relaxed in the canonical ensemble (NVT) or micro-canonical ensemble (NVE). The volume of a single PE chain is taken as the chain length multiplied by a cross-sectional area of 18 Å^2.4,5 In fact, the cross-sectional area would change slightly under torsion or stretching. However, to better compare the thermal transport of various structures under torsion or stretching, the cross-sectional area of one chain is considered as constant. For multi-chain structures, their volumes are determined by multiplying the number of chains by the volume of single chain.

Figure 2 shows the TC of suspended PE strands and the corresponding structures under torsional and stretching effects. The error bar of \( \kappa \) represents the standard deviation of eight realizations with different initial velocity conditions. Figure 2(a) shows the TC of suspended original polyethylene strands without torsional or stretching loading. Based on Figure 2(a), a single chain has a TC of around 60 W/(m K). The TC of the original PE strands is not dependent on the length. It shows good agreement with the results in others’ work,4,8,10,23 with more details shown in the supplementary material. It is worth noting that the TC of the original PE strands decreases weakly as the chain number increases, indicating that weak van der Waals interactions between chains in the original PE strands introduce slightly more phonon scattering that weakens the heat transport of PE strands in turn.

Figure 2(b) shows the TC of torsional PE strands versus torsional angles. The TC of single torsional PE chain decreases slightly as torsional angle increases. The decreasing TC of a single torsional chain is mainly attributed to the phonon scattering caused by increasing segment disorder. This is because a single torsional chain still exhibits good orientation, and the same box length ensures negligible strain effect. The torsion effect slightly increases segment disorder in the carbon chains and leads to moderate reduction of TC. It can be demonstrated in the following analysis of various torsional patterns. Torsional PE strands consisting of three or five chains show a different phenomenon, in that their TC increases slightly when the degree of torsion is 360°/20 nm. This abnormal increase is attributed to two mechanisms. On the one hand, the torsional effect limits atom vibrations and reduces the segment disorder along the chains. On the other hand, PE chains are tightened up to some extent as the torsional effect increases their length slightly.7 However, a visible drop is observed as PE strands are twisted by 720°/20 nm and 1080°/20 nm. It demonstrates that strong coupling between chains is not always beneficial to heat transfer.

![FIG. 1. Schematic views of various typical PE structures. (a) PE strands consisting of several suspended PE chains; (b) a single torsional PE chain; (c)–(f) are torsional PE strands consisting of two, three, four, and five chains, respectively.](image1)

![FIG. 2. TC of suspended PE strands and corresponding structures under torsional and stretching effects. The default length of PE chains is fixed as 20 nm. (a) TC of original suspended PE strands versus chain length; (b) TC of torsional PE strands versus torsional angles; (c) TC of torsional PE strands versus chain number at different torsional angles; (d) TC of torsional and stretching PE strands versus strain rate at different torsional angles, where the chain number is fixed as three.](image2)
Figure 2(c) shows the TC of torsional PE strands versus chain number at different torsional angles. As analyzed above, the torsional effect results in tightening up the PE chains, increasing coupling interactions between chains and reducing segment disorder. All these three effects become stronger as the chain number increases, especially for the outside PE chains. The strain effect of PE chains caused by torsional loading improves heat conductance. Reduction of segment disorder reduces the defects and structure disorders within PE chains. However, the increasing coupling between chains introduces more phonon scattering. The combination of these three effects determines the TC trend of torsional PE strands. When the chain number is less than four, the increasing strain effect and decreasing segment disorder enhances the heat conduction of strands. However, when the chain number is larger than four, the strong coupling between chains induces more phonon scattering and draws the TC down. The 720°/20 nm torsion is supposed to produce more phonon scattering than 360°/20 nm torsion as the coupling effect is much stronger.

It was shown that heat conduction of PE could be considerably enhanced by mechanical strain.9,13,26–28 Because stretching could improve the orientation order and crystallinity of polymers, it increases bonding interactions and leads to a larger phonon mean free path.23,29 Figure 2(d) exhibits the TC of torsional and stretching PE strands. It was shown that the TC of both original and torsional PE strands consisting of three chains is improved remarkably by stretching. The torsional PE strands have a better heat-conducting ability than the original PE strands under strain effect because the torsion produces a pre-tightening force between adjacent chains. The force enhances the rigidity of PE strands; thus, the strain effect can be more significant for torsional PE strands. Although torsion alone can only slightly improve the TC of PE strands, the combination of torsion and stretching is able to achieve a remarkable enhancement in thermal conduction. In addition, the combined effect is superior to each single effect of tension. Simulation details about the stretching process and ultimate strain are shown in the supplementary material.

To further reveal the impact of torsion and stretching on the TC of PE strands, we employ phonon power spectra to analyze their thermal conduction behaviors. The power spectra reveal phonon mode changes introduced by torsional and stretching effects.30,31 In the simulation, we calculate the velocity auto-correlation functions (VACF) of all atoms in PE strands. Their phonon power spectra are then extracted from the VACF using the fast Fourier transform.

Figure 3 shows the power spectra of various PE strands. Based on Figure 3(a), the phonon spectra of torsional PE strands and original PE strands overlap across the entire frequency range. There is a difference in the power spectra between original and torsional structures because of the torsion-induced strain. Thus, it is reasonable to believe that
torsion alone could make a modest enhancement in TC. At the same time, it is amply demonstrated that torsional loading does not introduce more phonon scattering in the longitudinal direction of PE strands. However, as shown in Figure 3(b), the phonon spectra of stretching PE strands apparently exhibit redshift, especially over the frequency range of 20–60 THz. Generally, the low-frequency phonons play a crucial role in thermal conduction due to their high group velocities and long mean free paths. Therefore, the stretching effect is able to improve the TC of torsional PE strands significantly. The higher TC of four torsional chains is mainly attributed to the existence of more low-frequency phonon modes in carbon atoms as its torsion-induced strain is larger than that of three torsional chains. More details are shown in Figures 3(c) and 3(d).

In the above discussions, there are just two torsional modes, including single-chain torsion and strand torsion. The thermal conducting capabilities vary with each torsional mode. Therefore, the TC may have a certain dependence on torsional modes. Figure 4 shows the TC of typical PE strands at various torsional patterns and their quantitative analysis. The torsion processes of single PE chains and PE strands are denoted by black and red arcs with torsional directions, respectively, as shown in Figure 4(a). Figure 2(b) indicates that torsion reduces the TC of a single PE chain, but it increases that of PE strands when the torsion degree is $360°/20\,\text{nm}$. As a result, the clockwise pair strand has a larger TC than the natural two chains, but the two-clockwise chains pattern has a lesser TC than the natural two chains. In addition, the clockwise-torsional two-clockwise chains pattern has the lowest TC, while the rope-like pair strand has the highest TC.

The carbon chain length of PE chains and the potential energy of van der Waals interactions between two chains are adopted to estimate the strain of chains and coupling strength between chains, as shown in Figure 4(b). Results show that PE chains within all torsional strands are longer than those within natural two chains ($20.62\,\text{nm}$), especially for clockwise pair strand ($20.68\,\text{nm}$) and rope-like pair strand ($20.70\,\text{nm}$). It proves that a weak strain effect does exist in torsional chains and strands. The classical 12–6 Lennard-Jones potential equation is adopted to calculate the van der Waals potential energy between two chains. It is found that the rope-like pair strand exhibits the weakest interaction ($-3.42\,\text{eV}$) among all patterns, even lower than that of natural two chains ($-3.66\,\text{eV}$) due to its special configuration. In contrast, the clockwise-torsional two-clockwise chains pattern has the strongest coupling strength ($-4.04\,\text{eV}$). To further explore the torsion effect on PE strand configuration, we use the angle and dihedral density distribution of carbon chains to evaluate the segment disorder along the chain, as shown in Figures 4(c) and 4(d). According to the bond angle density distribution of carbon chain, it is found that there are some small abnormal peaks in natural two chains and two clockwise chains. These peaks represent the segment disorder and structure defects. We can also find that there are small abnormal dihedrals in Figure 4(d), especially for two clockwise chains. It suggests that most phonon scattering
comes from the segment disorder regions where these abnormal angles and dihedrals happen. The existence of abnormal angle and dihedral density distribution is the main reason for lower TC values in a single torsional chain compared to the original single chain. The distribution results prove that the torsion for a pair of chains is beneficial to reduce the disordered segments.

Combining the above three effects, the rope-like pair strand achieves the highest TC since it has the longest carbon chain, the weakest coupling strength between chains, and nearly no abnormal segments along the chain. The TC of clockwise pair strand follows the rope-like pair strand as it has slightly higher van der Waals potential energy (−3.85 eV). The reason for lower TC of two clockwise chains is related to the abnormal segments produced by twisting single chains. In addition, the poor TC of clockwise torsional two clockwise chains pattern is mainly owing to the strongest coupling strength (−4.04 eV) among these five patterns. Some abnormal peaks still exist between 120° and 140° in the dihedral distribution, despite the two torsional chains have been twisted to a strand. The results illustrate that, for practical applications, more attention should be paid to the clockwise pair strand pattern and the rope-like strand pattern.

This work numerically investigates the TC of polyethylene strands under torsional and stretching effects by equilibrium molecular dynamics simulations. We systematically study the dependence of the TC of PE stands on the length, torsional angle, chain numbers, and strain rate. It is found that torsion reduces the TC of single PE chain as the torsional angle increases, but it could enhance the TC of PE stands slightly when the torsion degree is 360°/20 nm. In addition, the TC of torsional PE stands could be remarkably improved by stretching. Finally, the rope-like torsional strand without single-chain torsion can significantly improve the TC of PE stands compared with that of original ones. In conclusion, it is believed that the combination of torsional effect and stretching effect opens another avenue to improve the thermal conductivity of polymers. This is probably a promising technology, as the torsion method is expected to make full use of the high thermal conductivity of PE nanowires to produce bulk thermal conductive materials.

See supplementary material for simulation and calculation details. This material is available free of charge via the Internet.

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