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Thermal Conductivity of Amorphous and Crystalline Polyethylene: A Molecular Dynamics Study

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Abstract: In recent years, driven by rapid advances in polymer thermal applications such as thermal interface and thermoelectric materials, the complexities of heat transport in polymers have gained substantial attention. However, systematically investigating thermal conductivity across different polymer states remains a substantial challenge. Thus, we present a method for studying thermal conductivity in amorphous and crystalline polyethylene (PE) via molecular dynamics simulations. We investigate temperature, chain length, chain quantities, and tensile strain effects. Our results reveal a distinct trend in PE's thermal conductivity—initial increase followed by decrease. Chain length correlates positively, while chain counts correlate negatively with thermal conductivity. Additionally, stretching and crystallization notably enhance PE's heat transport, mainly due to optimized chain arrangement. This study comprehensively assesses diverse factors influencing PE's thermal conductivity, offering practical guidance for future experiments to enhance polymer thermal conductivity.

1. Introduction

These years, with the development of polymer science, a large number of polymers have been developed and proceed to become products commonly used in our daily life. However, the intrinsic low thermal conductivity limits its application in some fields like polymetric heat exchange devices, thermoelectric materials, and thermal interface materials.[1,2] Polymer materials possess distinct advantages when compared to conventional metal heat-conducting materials. These advantages include high toughness, corrosion resistance, low density, and ease of processing. Additionally, polymer materials can effectively compensate for the limitations of metal materials in terms of corrosion resistance. The extensive application prospects of polymers can be considerably enhanced if their thermal conductivity is improved. Hence, it holds immense importance in both theoretical research and engineering applications to explore efficient approaches for enhancing the thermal conductivity of polymers through the investigation of their thermal conductivity characteristics. Research has demonstrated that the heat conductivity of polymers is greatly influenced by the molecular arrangement of their structure.[3] The occurrence of tangles, cavities, and impurities within the molecular chains leads to notable phonon scattering and restricts thermal conduction. Conversely, enhancing the neat extent of molecular chain alignment in bulk polymers, specifically when the polymer chains are straightened through external force and organized in a systematic fashion, can greatly enhance the thermal conductivity.

Currently, the commonly used polymer ordering processing methods include electrospinning, nanoscale templating and mechanical stretching. Park et al. conducted electrostatic spinning on pure polyvinyl alcohol (PVA) to produce nanofibers. Their obtained nanofibers exhibited a thermal conductivity of 1.23 W/mK, a value that is six times more than that observed in bulk PVA. The observed enhancement in heat conductivity of the polymer was explained to the concurrent increase in its crystallinity.[4] Singh et al. employed the nanoscale template approach to synthesize amorphous nanofiber networks from a polythiophene melt. As a result, the synthesis yielded pure polythiophene nanomaterials exhibiting a thermal conductivity of up to 4.4 K/mK, which exceeds the thermal conductivity of bulk polythiophene by a factor of 20.[5] Apart from that, Shen et al. employed a two-step heating technique to elongate PE fibers, achieving a stretch ratio of 400. This process was undertaken to produce ultra stretched PE nanofibers possessing a remarkable thermal conductivity of 104 W/mK. which surpasses that of more than half of the metallic materials. The authors attribute this exceptional thermal conductivity to the reconfiguration of PE chains, resulting in a structure that closely resembles that of an ideal single crystal.[6]

It can be seen from above research that the thermal stretching method achieves higher thermal conductivity and is easy to operate compared to the electrospinning and nanoscale template methods. However, the experimental method cannot accurately observe the internal microstructure of the material, nor can it achieve uniform control of the strain rate. Therefore, the experimental methods have not been able to accurately study the effect of stretching conditions on the microstructure and thermal conductivity of materials. With the advancement in computer technology, computational simulations to study the thermal conductivity of polymers have also made great progress. Zhang et al. conducted molecular dynamics simulations to manipulate the rigidity of molecular chains and discovered a transition in PE from isotropic to anisotropic behavior. This transition was accompanied by a significant increase in thermal conductivity, approximately an order of magnitude increase.[7] The heat conductivity of branched PE chain was examined by Luo et al., with a focus on factors such as chain length, arrangement of branches, and type of branches. The findings indicate that the presence of branches has a significant impact on the thermal conductivity of PE. When the density of ethyl branched chains exceeds 200 fragments consisting of eight ethyl groups, the thermal conductivity of PE with ethyl branches decreases to a value that is approximately 40% of the thermal conductivity seen in the original PE chain.[8] To present, the majority of molecular dynamics investigations pertaining to the heat conductivity of polymers have mostly focused on polymer fibers and single chains. Comparatively, there have been less research conducted on bulk amorphous polymers. Moreover, the studies typically exhibit a lack of comprehensiveness since they just solely focus on one or two influential aspects.

In this paper, detailed research about the thermal conductivity of PE will be investigated. The amorphous PE systems with different chain length and number of chains have been modelled. And the thermal conductivity would be tested in the range of 200 K - 600 K. Additionally, the impact of tensile strain was studied by stretching the system to different length. Finally, the crystalline PE systems was also built and the strain dependent thermal conductivity was explored.

2. Systems and Methodology

2.1. Research Content

This research mainly focuses on diverse factors that may affect the thermal conductivity of PE. At first, amorphous PE systems with different chain lengths were built with 30 chains, as shown in Figure 1. The four systems contain 60 to 120 carbon atoms severally in each of their chains were built to search for the influence of chain length. Then, for analyzing the effect of chain number, PE systems have 10, 30, 50 and 70 chains with 100 carbon atoms per chain were constructed. At the same time, the thermal conductivity for different temperatures from 200 to 600K was simulated for all the PE systems. After that, the PE system, which consists of 30 chains with 100 carbon atoms in each chain, was stretched along the z-axis of the simulation box under different strain conditions: 0.25, 0.5, 0.75, and 1. Apart from the amorphous PE systems mentioned above, a crystalline PE system was also built and elongated with 0.1 and 0.2 strains to investigate how the thermal conductivity would alter in the crystalline structure.

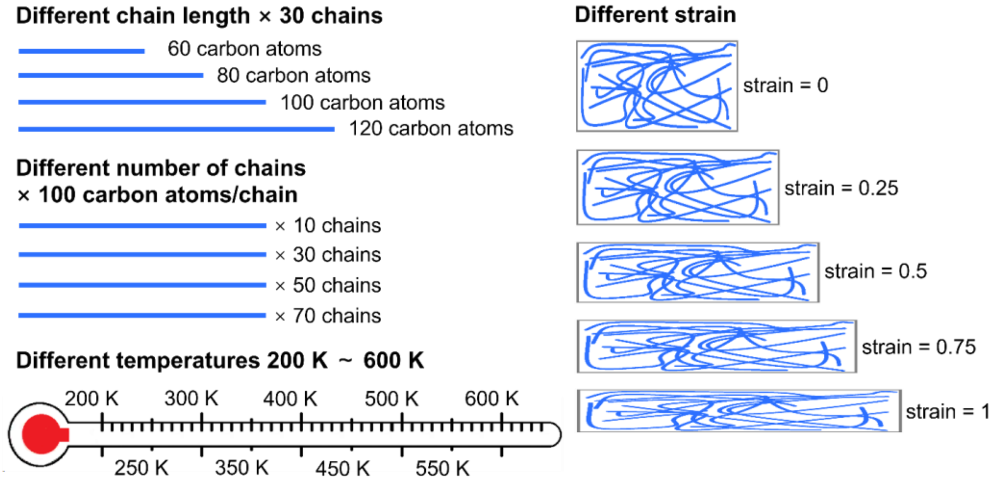

Figure 1: Schematic diagram of the main research content.

2.2. Molecular System Construction

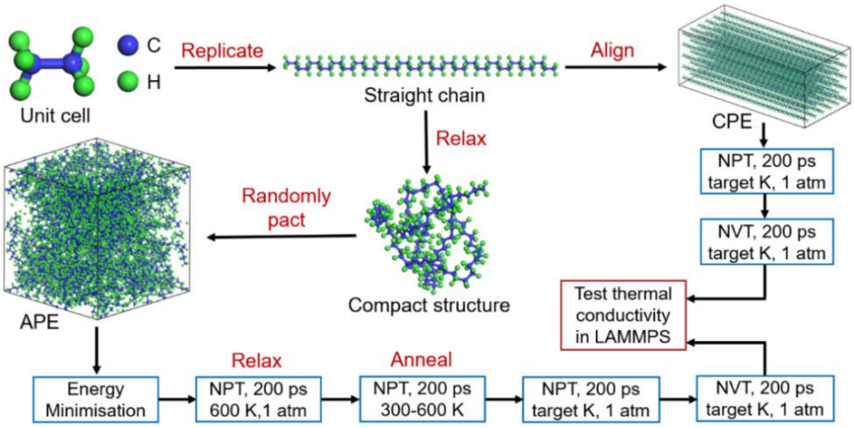

Figure 2: Flowchart for modelling and relaxation of PE.

The molecular system building processes were all in Materials Studio. As shown in Figure 2, a unit cell for a PE polymer chain was first built before being replicated to form a straight PE chain. Then the single chain was used as the raw component to build the amorphous PE (APE) and crystalline PE (CPE) systems, respectively. To create an amorphous PE system, the linear PE chains were initially allowed to relax for a designated duration, facilitating the development of a condensed structure. Subsequently, a number of these compact chains were tightly packed within a simulation box. For reaching the equilibrium state, the system was first energy minimized, followed by relaxation in NPT ensemble for 200 ps at standard atmospheric pressure. To avoid the energy of the system being trapped in the local minimum, the system was annealed between 300 K and 600 K for five cycles. Finally, before testing the thermal conductivity of the system, it was put in NPT and NVT ensemble under target temperature for 200 ps sequentially. As for the construction of a crystalline PE system, 30 straight PE chains with 50 degrees of polymerization for each chain were aligned in a supercell and parallel to each other. After that, the simulation system was relaxed in NPT and NVT ensemble for 200 ps to achieve an optimized structure, followed by finally sent to test the thermal conductivity.

2.3. Thermal Conductivity Test

In this project, the thermal conductivity for all the systems was tested by the Muller Plathe method in the large-scale atomic/molecular massively parallel simulator (LAMMPS).[9] This approach is one of the reverse non-equilibrium molecular dynamics (RNEMD) simulation methods. According to the Muller Plathe method, the simulation box was cut into 20 chunks with equal volume along the z-axis, which is the direction to test heat transfer in this research, as Figure 3(a) shows. Then the first and the eleventh chunks were set as the cold and hot regions correspondingly. In each 10 timesteps, the hottest atoms in the cold region would exchange their kinetic energy with the coldest atoms in the cold region. After a period of time, the temperature distribution in the box for the area between the cold and hot zones showed a trend of temperature gradient along the z-axis, like the form in Figure 3(b).

For calculating the thermal conductivity, the formula comes from Fourier's law of heat conduction[10]:

$$\kappa = -\frac{J}{\partial T/\partial z} \tag{1}$$

$$J = \frac{E}{2tA_{xy}} \tag{2}$$

Where κ is the thermal conductivity coefficient, $\partial T/\partial z$ means the temperature gradient along the heat transportation direction, and J indicates heat flux. In equation (2), E denotes the cumulative exchanged energy between the hot region and cold region in a period of time, t is the simulation time, and A_{xy} indicates the cross-sectional area in the xy plane. It should be noted that the 2 in the denominator part of the formula is caused by the periodic boundary condition along z-axis.

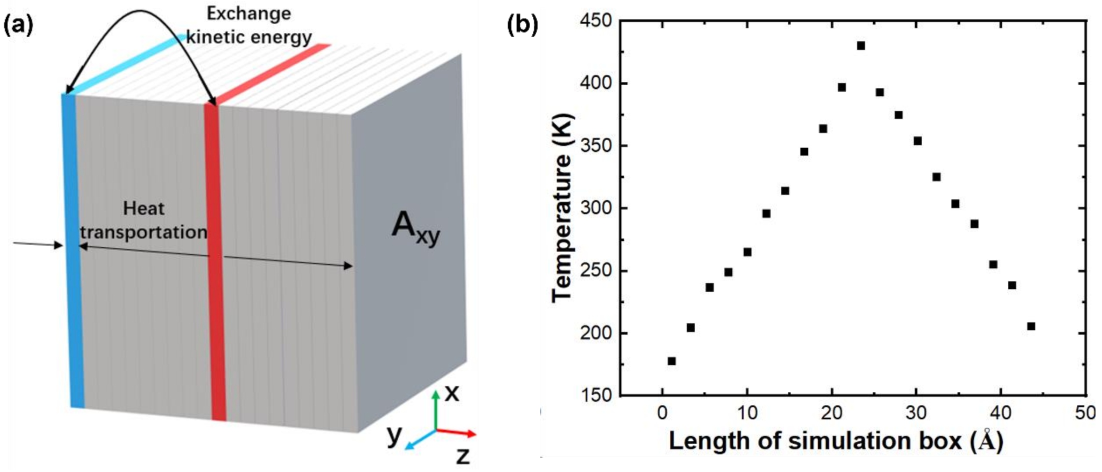

Figure 3: (a) Schematic diagram of the principle of Muller Plathe algorithm; (b) Temperature distribution of chunks along the z-axis of simulation box.

In the RNEMD simulation of this study, the PE system was first kept simulated for 10 ps under NVT ensemble to ensure the system had achieved a stable state. Then the system was divided into 20 chunks, and the energy exchange between hot and cold regions was sustained for 20 ps under the

NVE ensemble to equilibrate the system. After that, the system was simulated in an NVE (constant number of atoms, volume, and energy) ensemble for another 20 ps to collect heat flux data and calculate the value of thermal conductivity. The polymer consistent force field (PCFF) was adopted to describe the interatomic force interactions of PE system in this work. This force field has been utilized well in various polymer investigations, such as polylactic acid[11] and epoxy resin[12]. With the aim of minimizing errors and generating error bar graphs, the analysis was conducted five times with different initial velocities to test the thermal conductivity.

2.4. Mean Square Displacement

Mean square displacement (MSD) is a commonly employed method for determining the phase transformation and diffusion characteristics of materials.[13] It quantifies the extent to which the position of a particle deviates from the reference point as time progresses. The calculation formula of MSD is as follows:

$$\mathrm{MSD}=\frac{1}{N}\sum_{i=1}^{N}|r_i(t)-r_i(0)|^2 \tag{3}$$

In which N reflects the total number of particles that need to be measured, $r_i(0)$ represents the initial coordinate of the i-th particle, and $r_i(t)$ shows the position of this particle at time t.

3. Results and Discussions

3.1. Temperature and Chain Length

At first, an investigation is conducted to examine the impact of temperature on the thermal conductivity of PE system. It could be seen from figure 4(a) that when the temperature gradually rises from 200 K to 600 K, the thermal conductivity exhibits an initial increase followed by a subsequent decrease, with the transition occurring at approximately 350 K. The increase of thermal conductivity from 200 K to 350 K may be attributed to the change of polymer chain morphology. At low temperatures, the increment of temperature would enhance the mobility of chains and allow them to fill the empty spaces between chains, resulting in a more uniform distribution. Therefore, the better-intertwined chains would increase the interchain interaction and result in a larger interchain contact area, thereby facilitating efficient interchain thermal transportation. As for the decrease of thermal conductivity over 350 K, the observed phenomenon is caused by the lower density of the polymer system resulting from thermal expansion, as shown in Figure 4(b). In the wake of the increase in temperature, there is a notable expansion in the spacing between chains which makes the strength of interchain van der Waals interaction become much weaker. Hence, the thermal conductivity exhibits a declining trend with the growing temperature.

Figure 4(c) shows how thermal conductivity changes with the chain length. It is evident that as the carbon atoms in each chain increase from 60 to 120, there is a corresponding increase in thermal conductivity. The rationale for that is longer polymer chains have the ability to entangle with each other in a complicated configuration. As the length of the chain increases, a larger compact area could be formed between PE chains. Consequently, this enhances interchain interaction and leads to an improvement in thermal transport efficiency. Besides, a long polymer chain means a long heat transport path. The most efficient heat transfer in the PE system is achieved through intra-chain phonon transport facilitated by carbon-carbon covalent bonds is the most effective heat transfer approach for the PE system. Therefore, the longer polymer chain implies heat can be efficiently transferred over a further distance.

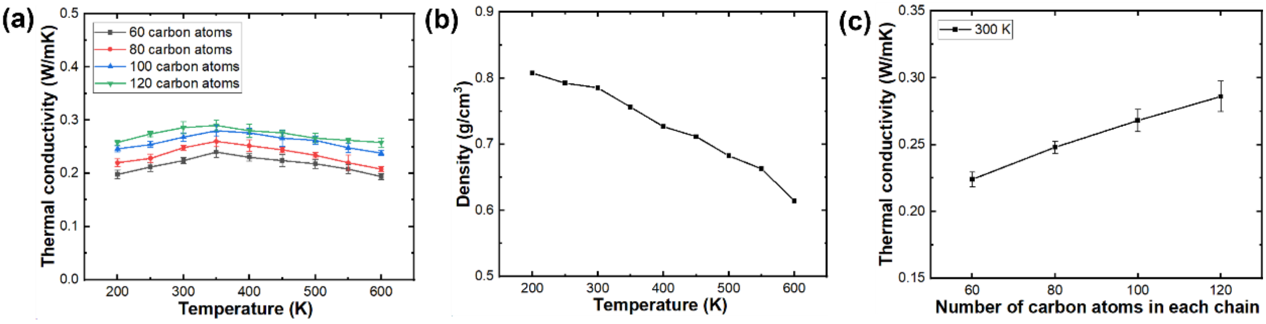

Figure 4: (a) Thermal conductivity of amorphous PE change with chain length at different temperatures; (b) Density of amorphous PE change with temperature; (c) Thermal conductivity of amorphous PE change with chain length at 300 K.

3.2. Number of Chains

Regarding the impact of the number of chains, it could be seen from Figure 5(a) and (b). The thermal conductivity keeps an increasing trend when the number of PE chains in the system falls within the range of 10 to 70. The mechanism of that can be attributed to the reciprocal interference effect between neighboring chains. The vibrational behavior of each chain is constrained by the surrounding chains, the increase in the chain number restricts the motion of the atoms, thereby reducing the thermal conduction of phonons resulting from interatomic collisions. Besides, the presence of a greater number of chains in the system introduces increased complexity to the vibrational modes occurring between molecules. Thus, this leads to a higher propensity for phonons scattering with defects, impurities, and other phonons. These scattering would subsequently impede the transmission of phonons, hence resulting in a decrease in thermal conductivity. Furthermore, it should be noted that the dimensions of the system would expand according to the number of chains present, causing an increased distance for heat transfer across the system. As a result, there is an increase in the frequency of interchain heat transfers, thus reducing the overall heat transfer efficiency.

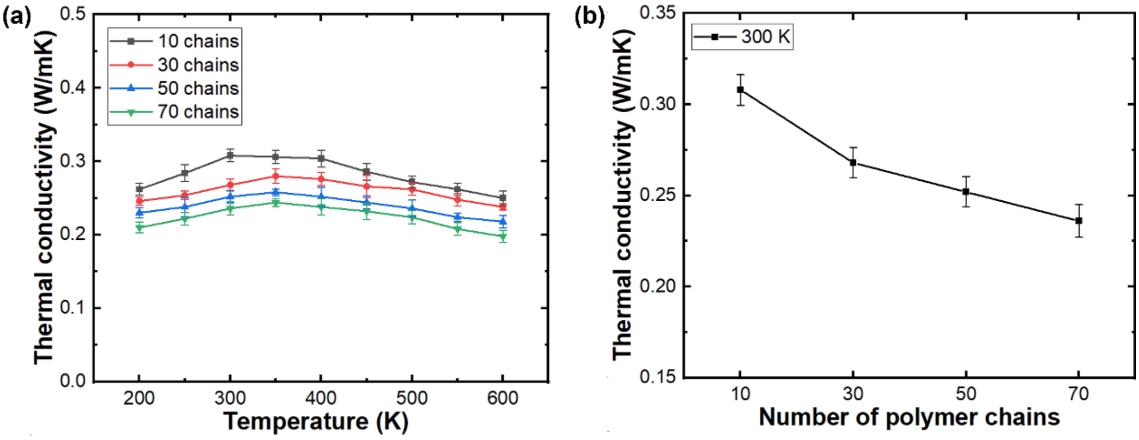

Figure 5: (a) Thermal conductivity of amorphous PE change with chain numbers at different temperatures; (b) Thermal conductivity of amorphous PE change with chain numbers at 300K.

3.3. Tensile Strain

As for the research about stretch, four different stains from 0.25 to 1 were applied to the system. It could be found in Figure 6(a), when the PE model undergoes a stretching process resulting in a doubling of its original length, there is a significant enhancement in the thermal conductivity, reaching nearly threefold. This observation reflects the notable impact of stretching on the thermal conductivity of the PE system. The rationale of it is that stretching deformation compels the polymer chains to align in the direction of stretching, thereby inducing chain alignment. When a sample is stretched, the proportion of backbone carbon bonds that are orientated in the stretching direction become higher, as shown in Figure 6(b). Therefore, the thermal conductivity becomes much higher when the PE system is stretched along the z-axis. Apart from that, applying mechanical strain causes the polymer chains to undergo extension in the direction of tension. The efficiency of heat transmission is greatly enhanced when it occurs along aligned chain structures compared to the randomly tangled configuration, primarily due to the reduced phonon scattering that takes place in the former. Some experimental research also demonstrated a comparable increase in the thermal conductivity of PE along the direction of draw.[14]

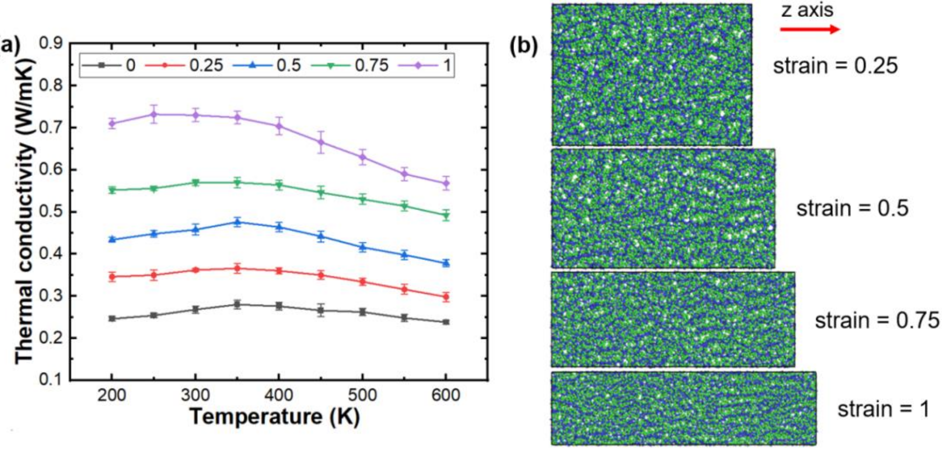

Figure 6: (a) Thermal conductivity of amorphous PE change with change with various tensile strain at different temperatures; (b) Morphology of amorphous PE with different strains.

3.4. Crystalline PE

Finally is research about the performance characteristics of crystalline PE. From Figure 7(a), the results indicate that the crystalline PE has much larger thermal conductivity compared to its amorphous counterpart, exhibiting an increase of about 10 times. The crystalline PE was also subjected to various strains, resulting in an increase in thermal conductivity to higher magnitudes. The significantly high thermal conductivity of crystalline PE can be assigned to the neater molecular arrangement and closer intermolecular interactions. The presence of such an ordered molecular arrangement fosters the more efficient transfer of thermal energy by phonons. In contrast, amorphous PE exhibits a more disordered molecular arrangement, contributing to a higher prevalence of defects in the system. Hence, phonons experience a greater number of obstacles and scattering during the process of heat transport, leading to a reduction in thermal conductivity. At the same time, the density of crystalline PE is noticed to be higher than the amorphous PE. That is caused by the alignment of the PE chains in a more compact manner, thereby narrowing the inter-chain spacing. Greater closeness among chains promotes a higher degree of interchain interaction, hence further augmenting the overall capacity for heat transmission.

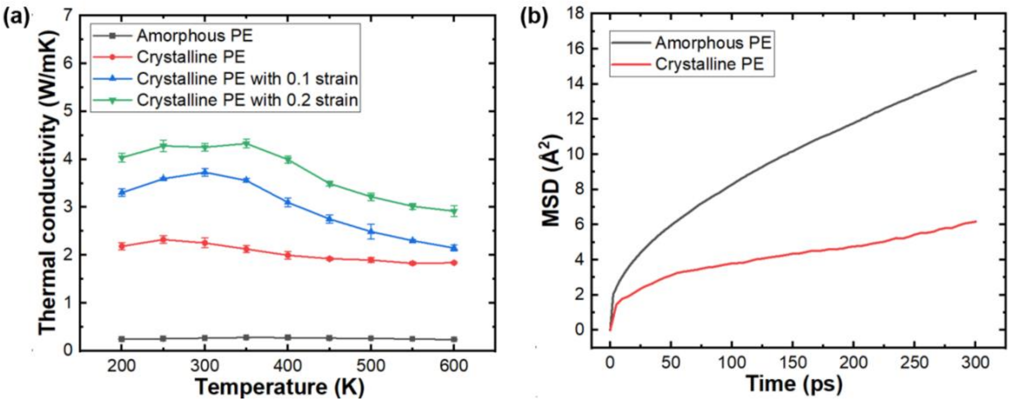

Figure 7: (a) Thermal conductivity of amorphous and crystalline PE change with tensile strains at different temperatures; (b) Mean square displacement for amorphous and crystalline PE.

MSD is able to provide insights into the diffusion behavior of atoms within a given system. Here in Figure 7(b), it is used to measure the motility of carbon atoms in the amorphous and crystalline system at 300 K. The results reveal that the MSD for the amorphous PE has a notably steep curve. That is caused by the loosely organized structure in amorphous PE. The interchain interaction is weak, meaning that molecules are not considerably constrained in the system, and therefore, these molecules possess greater freedom to vibrate and move which leads to elevated MSD value. For the crystalline PE, it is observed that MSD decreases significantly, the resulting curve exhibits a more gradual slope. The rationale behind that is the specific alignment of chains in a tighter form, hence significantly restrict the mobility of atoms in the chains. The system experiences a decline in atomic vibrations, leading to a drop in the amount of phonons. Consequently, the scattering of phonons owing to mutual collisions between them is diminished, explaining the observed rise in thermal conductivity.

4. Conclusion

RNEMD simulation was performed in this study to analyse the thermal conductivity coefficient of PE system. Results indicated that the thermal conductivity of PE shows an increasing trend at low temperature and gradually drop at higher temperature with a transition temperature at about 350 K. The longer chain length is good for improving thermal conductivity while the number of chains in the system gives the opposite effect. In addition, tensile stretch is able to greatly enhance the thermal conductivity of PE system. The value achieves nearly threefold when the strain is 1. Furthermore, the crystalline PE system was also constructed, and various stresses were applied on it. The outcome suggests that the thermal conductivity of crystalline PE is almost ten times greater than the amorphous system and its value could even be higher after stretching. That’s because the neatly chain alignments allow longer distances for intrachain heat transformation based on carbon backbone. Therefore, the thermal conductivity of PE can be controlled to some extent by mediating these factors.

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