THERMAL CONDUCTIVITY ENHANCEMENT OF POLYMERS VIA STRUCTURE TAILORING

Shen Xu,† Jing Liu,† & Xinwei Wang

1School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science, Shanghai 201620, China
2Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, USA
3College of New Materials and New Energies, Shenzhen Technology University, Shenzhen 518118, China

†Shen Xu and Jing Liu are equal contribution authors
*Address all correspondence to: Xinwei Wang, Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, USA; Tel.: +1 515 294 8023; Fax: +1 515 294 7771; E-mail: xwang3@iastate.edu

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Polymers are usually known for their low thermal conductivity. However, the demand in industries for polymers with high thermal conductivity has increasingly grown due to their low density, low cost, flexibility, and good environmental resistance compared with conventional substances of high thermal conductivity. Composites filled with high thermal conductivity nanofillers will increase thermal conductivity \((k)\); however, it has been clearly observed that the mechanical properties will deteriorate along with this process. Instead, increasing the intrinsic thermal conductivity of polymers themselves is more important. This review focuses on the mechanism of increasing \(k\) from the perspectives of polymer intrinsic structure tailoring: crystallinity, orientation of the crystallites, crystalline grain size, and alignment of the molecular chain in the amorphous region. Structure tailoring methods of increasing/improving these four factors are critically reviewed and discussed. Accurate thermal characterization methods are critically reviewed for these structure-tailored polymers in low dimensions. The transient electro-thermal and pulsed laser-assisted thermal relaxation techniques provide some of the best and most accurate thermal conductivity measurements with high physics control.

KEY WORDS: structure tailoring, thermal characterization, polymers, thermal conductivity

1. INTRODUCTION

1.1 High Demand for Polymers with High-Thermal Conductivities

Polymers are preferable in current industrial applications due to their low cost, flexibility, good environmental resistance, etc.; however, most of them are regarded as thermal isolation materials because their low thermal conductivity \((k)\) is usually lower than 0.5 W/(m·K) (Han and Fina, 2011). For example, among the major industrial polymers in use, acrylic glass [poly(methyl...
methacrylate), an alternative optical material, has a $k$ value of $\sim 0.2$ W/(m·K). Other polymers also have low $k$ values. For example, the $k$ value for nylon and polyvinyl chloride, a flame retardant material, is 0.25 W/(m·K). The $k$ value for polyethylene (PE), a polymer frequently used in food industry, is 0.3–0.5 W/(m·K), and the $k$ value for polypropylene (PP) is 0.17–0.22 W/(m·K) (Engineering ToolBox, 2011). The low thermal conductivity of polymers is partly due to the low crystallinity of their internal physical structure. The typical crystallinity of regular bulk polymer is in the range of 10%–80%.

However, polymers with high thermal conductivity are currently in high demand in industries in the field of electronic packaging in microelectromechanical systems, especially with the miniaturization of electronic devices (Zweben, 2005). The high-power density of devices generates a large amount of heat on a small scale and demands an efficient high heat dissipation rate. Meanwhile, good electric isolation is needed to maintain good performance of devices. Thus, high thermal conductivity polymers are potential candidates instead of metallic materials for good thermal management purposes in miniaturized devices. In addition, the highlighted features of low mass density and high corrosion resistance of polymers can offer better performance than conventional metallic materials if their thermal conductivity meets the desired level. Take heat exchangers as an example (Chen et al., 2016c; T’Joen et al., 2009); although metallic materials are preferable in heat dissipations, their large mass and electrical conduction sometimes may not fit the situation. In the field of thermal protection (Crown and Batcheller, 2016), thermal protection on the human body has contradictory requirements of heat isolation and dissipation under ergonomics and physiological considerations. The material used should block high temperatures outside a protective suit but also be capable of conducting heat and humidity away from the human body. Also, a protective suit is expected to have low mass. In this case, an easily fabricated polymer with controllable high thermal conductivity is a good candidate for thermal protection. Thus, enhancement in the thermal conductivity of polymers is urgently needed in these fields (Guo, 2019).

### 1.2 Thermal Conductivity Enhancement in Polymer-Based Composites

In the past, researchers have made great efforts to increase the $k$ value of polymers through composition, such as embedding/dispersing high-$k$ fillers in a polymer base, including metallic particles (Chen et al., 2016b; Danes et al., 2003), ceramic particles (Kim et al., 2014; Kusunose et al., 2013; Sim et al., 2005; Zhou et al., 2009a,b), carbon nanotubes (Winey et al., 2007; Yu et al., 2016), and graphene (Diaz and Guo, 2019; Lin et al., 2015; Song et al., 2013). Chen et al. (2016) added single-crystalline copper nanowires of high-aspect ratio into epoxy resin to realize a thermal conductivity of 2.59 W/(m·K), which was eightfold higher than that of plain epoxy resin. To utilize the high thermal conductivity of ceramic particles, Kim et al. (2014) embedded boron nitride powder fillers into an epoxy-terminated dimethylsiloxane matrix. The surface of the boron nitride particles was hydroxyl-functionalized and doped with surface curing agents such that the ceramic particles could be chemically bonded with the epoxy resin. In this composite, the thermal conductivity was enhanced up to 70%. After their discovery, carbon nanomaterials became preferable since they exhibit the desirable physical properties of low density and ultrahigh thermal conductivity. Biercuk et al. (2002) prepared a single-walled carbon nanotube/epoxy composite with 1 wt% of unpurified carbon nanotube load and found a 125% increase in the thermal conductivity at room temperature. Song et al. (2013) bonded graphene flakes to 1-pyrenebutyric acid through $\pi-\pi$ stacking and added this nanocomposite into epoxy resin in order to increase the overall thermal conductivity of the resin to 1.53 W/(m·K). The
mechanisms of controllable enhancement of thermal conductivity in polymer-based composites, including filler loads, the morphology of fillers, and the interface between fillers and bases, either with or without the inter-filler networks, have been widely discussed and are summarized in some comprehensive review works (Chen et al., 2016a; Huang et al., 2018).

Adding high-$k$ fillers has been widely proved to be an efficient way to control and optimize the thermal conductivity of composite systems over pure polymer systems. However, as found in the literature, for most of the crystalline or semi-crystalline polymers, increasing the quantity of fillers will decrease their overall mechanical performance (Jordan et al., 2005). Furthermore, when the one-dimensional size of polymers changes from macroscale to micro/nanoscale, the fillers will largely decrease the strength in the mechanical behavior of polymers. Therefore, this significantly limits the application of fillers on a small-scale level. A more workable approach is to improve the $k$ value of polymers by tailoring their microscopic structure instead of using fillers. This review focuses on the physics and techniques used to significantly improve the $k$ value of polymers by tailoring their microscopic structures. The physics principles of structure tailoring are discussed in Section 2, and based on these principles the commonly used methods for structure tailoring and structure characterization are summarized in Section 3. Section 4 presents the advanced and efficient technologies used to measure the thermal properties of enhanced polymers, especially in relation to thin fibers and films at the micro/nanoscale.

2. PHYSICS UNDER STRUCTURE TAILORING FOR THERMAL CONDUCTIVITY ENHANCEMENT

When there is no embedded second material inside, the thermal conductivity ($k$) of polymers is significantly determined by its crystallinity, the crystal grain (crystallite) size, grain (crystallite) alignment/orientation, and amorphous regions connecting the crystallites, as well as the molecular chain length. Theoretical work on the $k$ value of polymers based on molecular dynamics (MD) simulation, or other methods using a single molecular chain, usually cannot consider all of these structural effects. As a result, the reported $k$ value sometimes even becomes divergent. Using the Green–Kubo approach and a modal decomposition method, Henry and Chen (2008) reported a $k$ value of $\sim 350$ W/(m·K) for PE. For PE polymer chains, a subsequent study by Liu and Yang (2012) pointed out that if there is no defect in the polymer chains, the $k$ value will continue to increase with the polymer length when phonon boundary scattering is lacking. In that work, it was reported that the anomalous heat diffusion and $k$ value increase with the polymer chain length ($L_0$) as $k = CL_0^a$, where $C$ is 19.58, $a = 0.382$, and $L_0$ is in nanometers. Such anomalous heat diffusion was also found for other different polymer chains, as shown in Fig. 1. This has been extensively studied and confirmed, and is termed anomalous heat diffusion (Li and Wang, 2003). Therefore, great caution should be exercised in reporting the intrinsic thermal conductivity of single polymer chains using MD simulations when no defect is present. The non-perfect structure of real polymer chains will significantly reduce the $k$ value. For instance, using MD simulation, Liu’s group discovered that kinks in PE molecular chains could significantly reduce the $k$ value (see Duan et al., 2019). For each kink in the PE chain, a thermal resistance of $\sim 3.7 \times 10^{-10}$ (m$^2$·K)/W arises. Therefore, the existence of kinks and their density can significantly affect the overall thermal conductivity of the PE chain. Despite some limitations in the theoretical studies, they still provide great insight into the mechanism of heat conduction in polymers, which could help in the understanding of experimental observations. Some caution needs to be taken when using theoretical predictions to predict the upper limit of the $k$ value of polymer chains.
As will be discussed in detail in Section 4.3 in the structure analysis based on phonon scattering using the thermal reffusivity theory, phonon scattering will include the phonon–phonon scattering (Umklapp scattering) and phonon–defect scattering. It is natural to reduce the defect scattering as much as possible in order to improve the thermal conductivity. However, when increasing the thermal conductivity, the crystalline grain orientation and amorphous region alignment should also be considered. To improve the $k$ value of polymers, four fundamental physics principles are usually taken into account. The first one is to improve the crystallinity level of the material since the crystalline structure has a $k$ value much higher than that of the amorphous region. At room temperature, PE of 81% crystallinity was reported to have a $k$ value 70% higher than that of 43% crystalline PE (Choy, 1977). If a polymer has a high anisotropic structure (which in most cases is true), the polymer chain direction will have a much higher $k$ value compared to other directions. When talking about increases in the value of $k$, here $k$ refers to the polymer chain direction. Such $k$ improvement can be significant when the crystallinity is increased from a very low level. However, when the crystallinity level reaches a high level, e.g., 90%, a further increase in crystallinity becomes more difficult and the corresponding increase in the $k$ value becomes very marginal. In polymers, amorphous regions usually have a thermal conductivity ($k_a$) several fold or orders of magnitude lower than that of the crystalline part ($k_c$, along the chain direction). Even a small portion of an amorphous region in the material will significantly reduce the overall thermal conductivity. For instance, an extreme case would be an amorphous region connected to the crystalline part in series in the polymer chain direction. If $k_a = 0.01k_c$, even when the amorphous region takes 10% volume, the overall $k$ value will only be 0.092$k_c$. This clearly illustrates the limitation of increasing the $k$ value by increasing the crystallinity. If the amorphous region is connected to the crystalline part in parallel, the overall $k$ value will be $0.901k_c$. In real situations, both parallel and serial connections co-exist (Zhu et al., 2017). Thus, if a strategy is taken to increase the crystallinity level in order to improve the value of $k$, it is best to reduce the amorphous region portion serially connected to the polymer chains. This serial- and parallel-connected structure analysis could also provide a quick theoretical estimate to check the validity of some of the claimed hyper-thermal conductivity of various materials not only limited to polymers.
Second, the orientation of the crystalline grains plays a critical role in determining the overall \( k \) value since crystal has a strong anisotropic nature of thermal conductivity. Aligning the high-\( k \) direction of nanograins along the same direction is critical to achieving a very high effective \( k \) value. This has been widely recognized when increasing the \( k \) value of low-\( k \) materials by dispersing some high-\( k \) particles, flakes, and rods. It is not only the \( k \) value of the material, but also the microscopic orientation that determines the overall thermal conductivity. In the work by Wang et al. (1999) on the \( k \) value of nanofluids, it was pointed out that nanoparticle chains/clusters will help improve the thermal conductivity of nanofluids more than nanofluids that have just simply dispersed nanoparticles. Subsequently, this mechanism was observed and proven in the work by Gao et al. (2009). Therefore, for polymers, if the stretching/drawing cannot simply increase the crystallinity, but makes the crystallites more aligned along the drawing direction, the final \( k \) value will be significantly improved. Here, a simplified model is taken to demonstrate this alignment effect. For a polymer that has a low crystallinity level (\( \phi \)) of 10%, in which the crystalline grains are randomly distributed within the material, the overall thermal conductivity \( (k) \) can be estimated using Maxwell’s equation as follows:

\[
k = k_a \left[ 1 + \frac{3(\alpha - 1)\phi}{(\alpha + 2) - (\alpha - 1)\phi} \right]
\]

where \( k_a \) is the thermal conductivity in the amorphous region \( (\alpha = k_c/k_a) \), and \( k_c \) is the effective thermal conductivity of the crystalline grains (considering the anisotropic structure). If we have \( \alpha = 10 \), then \( k \) will equal \( 1.24k_a \). However, if the crystalline grains are aligned along the heat transfer direction, and the polymer chain direction of the grains is also aligned along the heat transfer direction, the situation will change very much. The polymer chain direction thermal conductivity \( (k_{c,2}) \) usually is much higher than \( k_a \). Here, we take \( k_{c,2} = 20k_a \). Under such aligned situations, the thermal conductivity of the polymer will be \( k = \phi k_{c,2} + (1 - \phi)k_a = 2.9k_a \). This strongly demonstrates the importance of crystalline orientation in the overall thermal conductivity.

Third, even for the crystalline part, the grain/crystallite size could significantly affect the value of \( k \). This is due to the fact that if the grain has a small size (e.g., a few nanometers), the phonon mean-free path (MFP) (along the chain direction) will be significantly limited by the grain size and boundary scattering, thereby significantly reducing the thermal conductivity of the grain. Such a size effect, by the first order, can be expressed as \( l^{-1} = l_0^{-1} + l_g^{-1} \), where \( l \) is the phonon MFP in the crystalline grain, \( l_0 \) is the intrinsic MFP of the phonons, and \( l_g \) is the characteristic length of the grain. It should be noted that for a nanograin of a polymer, the grain size in both the directions parallel and normal to the polymer chain will affect the \( k \) value in the chain direction (Zhang et al., 2011; Zhong et al., 2004). For polymers, the atomic bonding between atoms along the chain direction (intra-chain) is covalent, and could transfer energy very fast from atom to atom. The interaction between chains is via the Van der Waals force, and is usually much weaker. Therefore, it is expected that the grain size in the direction normal to the polymer chain direction will have a much weaker effect on the thermal conductivity in the chain direction. Under the situation neglecting the inter-chain grain size effect, the effective thermal conductivity \( (k_{eff}) \) is related to the grain size \( (L) \) in the chain direction as \( k_{eff}/k_c = [1 + P \cdot (l/L)^{-1}]^{-1} \), where \( k_c \) is the thermal conductivity of defect-free infinitely large polymer crystal, and \( l \) is the intrinsic MFP (Zhang et al., 2011). Here, \( P \) is the correlation related to the boundary conditions of the crystallite. Figure 2, in relation to the effect of size, illustrates how the thermal conductivity changes with the length for a graphene nanoribbon of 1.99 nm width.
FIG. 2: Thermal diffusivity ($\alpha$) and thermal conductivity ($k$) variations against the graphene nanoribbon length [reprinted with permission from Zhang et al. (2011); © American Physical Society]

(Zhang et al., 2011). Such a strong size effect exists as long as the grain size (width and length) is comparable to or smaller than the MFP in polymer crystalline grains.

The fourth principle is to align the amorphous polymer region, especially the region connected in series with the crystalline part. This is different from the first principle previously discussed, which focuses only on increasing the crystallinity level. Since there are always amorphous regions in a polymer material (i.e., the material cannot be 100% crystalline), the amorphous region connected to crystallites in series in the polymer chain direction plays a critical role in limiting the heat conduction capability. This effect has been studied in detail by Zhu et al. (2017), as shown in Fig. 3. Since the polymer chains have intra-chain covalent and inter-chain Van der Waals bonds, the inter-chain thermal conductance usually is very small, and the thermal conductance along the chain is much higher. Therefore, it is very favorable to align the amorphous region among the crystallites in order to significantly increase the overall $k$ value. In the aforementioned theoretical work on the $k$ value of PE, only a single molecular chain was studied. Therefore, this prediction can also be applied to the amorphous chain’s $k$ value. If an amorphous chain is not straight, then the heat conduction along it will go through a relatively much longer path, making the effective $k$ value much lower. Such physics can also be used to explain the very low thermal conductivity/diffusivity of carbon nanotube bundles (Xie et al., 2018a) and graphene foams (Lin et al., 2013). As previously mentioned, the amorphous region connected in series with the crystallites in the polymer chain direction plays a critical role in determining the overall thermal conductivity. Therefore, aligning the amorphous chain in this region makes the most sense toward increasing the thermal conductivity. Some works that have reported significantly increased $k$ values of polymers upon drawing/stretching clearly confirm this amorphous alignment mechanism (Choy et al., 1997, 1999).
FIG. 3: Schematic illustration of the amorphous region alignment effect on the thermal conductivity of PE fiber: (a) amorphous region alignment after stretching ($\phi_{a,\perp}$, $\phi_{a,\parallel}$, and $\phi_c$ denote the volumetric fractions of the serial amorphous, parallel amorphous, and crystalline regions, respectively); (b) simplified thermal resistance network model to quantify the effect of various regions [$R_{a,\perp}$, $R_{a,\parallel}$, and $R_c$ are the thermal resistances of the serial amorphous, parallel amorphous, and crystalline regions, respectively; for a sample of the unit length and cross-sectional area: $R_{a,\perp} = \phi_{a,\perp}/[k_a(\phi_{a,\perp} + \phi_c)^2]$, $R_{a,\parallel} = 1/k_a\phi_{a,\parallel}$, $R_c = \phi_c/[k_a(\phi_{a,\perp} + \phi_c)^2]$, and $1/R_{\text{eff}} = 1/R_{a,\parallel} + 1/(R_{a,\perp} + R_c)$); (c) thermal conductivity variation against the fraction of the serially connected amorphous region to explain why the thermal conductivity increases when the crystallinity is reduced [reprinted with permission from Zhu et al. (2017); © American Chemical Society]

For increases in thermal conductivity, the intrinsic structure of the polymer itself also plays a critical role. Take PE as an example, the length of the molecular chain has a direct impact on the thermal conductivity. Short polymer chains tend to form small crystallites or crystallites with many dangling chain segments. A shorter chain will reduce the $k$ value of the crystalline region because of the short MFP, and a longer chain will introduce more defects inside the crystallites and on the crystallite boundary, limiting heat conductance. However, when the molecular chains are longer there will be fewer dangling chain segments, and thus fewer defects on the boundary. In addition, a polymer chain may be long enough such that both of its ends engage the crystallites, and the chain can conduct heat more efficiently than tangled tails of different chains. For polymers, the structure of the monomer itself is also critical for thermal conductivity. A general rule is that if the monomers have more branched/complicated structures (e.g., such as higher-order randomness), the overall thermal conductivity tends to be lower (Luo et al., 2017; Volume 27, Issue 5, 2020)
This is because the existing branched structures occupy the space between backbone chains and hinders the interaction between backbone chains, including the formation of crystallites (Zhang et al., 2018). This explains why PE has the highest thermal conductivity of the reported polymers. For copolymers, the junction of the chains makes the overall structure much less perfect, leading to much lower thermal conductivity (Luo et al., 2011; Tu et al., 2017; Zhang et al., 2014). First, this is because the junction causes significant local phonon scattering and reduces the thermal conductivity along the chain direction. Second, the junction itself makes it much less possible for single crystalline grains to form in the material.

Considering the four principles for increasing thermal conductivity, when the crystallinity is low it is easier to increase the $k$ value by increasing the crystallinity level. However, such a method will quickly see its limitation. Therefore, the crystalline orientation should always be considered when increasing the crystallinity. Sometimes, the orientation effect can be much more than the crystalline grain size effect. When the crystallinity reaches a high level, the amorphous region alignment method is the most promising way to increase the thermal conductivity since a further increase in crystallinity becomes difficult, and even with the same level of increased crystallinity the increase in thermal conductivity becomes very slow.

3. METHODS FOR STRUCTURE TAILORING

3.1 Structure Tailoring

Based on the aforementioned four mechanisms, tailoring the structure of polymers could increase the thermal conductivity of polymers. Diverse approaches have been proposed and developed to realize thermal conductivity enhancement of polymers. The most commonly adopted way is achieving crystallization in solidification from polymer melt. When the temperature is above the melting point, all of the molecular chains in the melt can move freely. A few chains randomly align in parallel due to thermal movement and offer seeds for nucleation in solidification. The remaining part of the chains and other chains will then align automatically around the seeds to form crystallites in the polymer. Compression molding is one of the common industrial techniques employing the solidification of polymers to produce bulk polymers. This method directly compresses the melt into a desired shape and releases the resulting bulk after it is cooled. The cooling process is critical in crystallite growth. Theoretically, the longer the cooling process lasts, the larger are the obtained crystallites (Kurtz, 2019). However, long cooling periods are not practiced in industrial fields. Another popular technique for fiber and film fabrication is injection molding. In this process, molten polymer passes through a nozzle that applies stress to the melt during its cooling. The forced alignment of the molecular chains and generated crystallites along the flowing direction increase the crystallinity and crystalline size in the resulting fibers and films. The temperature and flow rate are key factors affecting the crystallinity of the resulting products, both of which need to be controlled.

Nucleating agents can increase the crystalline growth rate and ease the polymer crystallization (Lotz et al., 2017). They function as nuclei in a polymer solution or melt, interact with molecules in the polymer, and start the polymer nucleation. Nucleating agents can be low molecular weight crystalline particles, crystalline polymers, and metal salts of organic acids that are crystalline at the melting point of polymers. Applying nucleating agents can increase the crystallinity of polymers; however, suitable nucleating agents for polymers vary from one type to another and their application is empirical to some extent. The development and dispersion of nucleation agents for industrial purposes still face major concerns.
Coating and deposition processes employ a substrate as the nucleating agent. Li and Yan (2011) reviewed the effect of the surface on epitaxial crystallization of polymers. On a flat surface, a crystalline substrate surface will restrict the crystalline orientation and structure in a grown polymer film when the crystalline polymer structure matches the substrate’s structure. This peculiar interaction is important for polymer crystallization on an amorphous structure. For curved surfaces, such as a fiber surface, the intrinsic surface characteristics, interface stress, and flow field should be taken into account when generating polymer crystallization. Wang et al. (2018) investigated semi-crystalline polymer thin films prepared by the physical vapor deposition method and controlled the film morphology and thermal properties of matrix-assisted pulsed-laser evaporation–deposited polyethylene oxide (PEO) films by tuning the temperature and substrate type. Confining environments are widely used to generate homogeneous nucleation in polymers (Dorenbos et al., 2002; Liu and Chen, 2010). Li and Zhang (2015) spin coated poly(3-hexylthiophene) (P3HT) film on a nanostructured pattern. A small amount of dissolved photoresist in 1,5-pentanediol offered nucleating agents and the nanopattern confined the crystalline growth direction. Nucleating agents and the nanopattern confined the crystalline growth direction achieved directional organic crystal fibers of 2 µm wide and centimeters long.

The spin-coating fabrication process can align molecular structures along the centrifugal direction to yield highly anisotropic mechanical and thermal properties of polymers. Feng and Wang (2011) fabricated highly anisotropic thin P3HT film using this technique. In their work, regioregular P3HT was first dissolved in a chloroform solvent, and spin coated on a glass plate at a high speed of 5000 rpm. The thickness of the P3HT films ranged from 20 to 40 µm. Different concentrations of the solution caused different film densities in the spinning/coating process. Based on these samples, the advanced thermal measurements obtained revealed the following trend: the overall thermal conductivity of the films became higher, while the overall thermal diffusivity was lower when the film was denser. Further detailed study showed that the molecular chain was forced to align along the centrifugal direction by the strong centrifugal force (Feng et al., 2013). The produced P3HT film had a strong anisotropic structure, and thus produced the thermal properties in the film. The thermal measurement results are shown in Fig. 4, where it can be seen that \( k \) values up to 3.18 W/(m·K) occur along the centrifugal direction. The \( k \) value was around 0.6 W/(m·K) in the in-plane direction perpendicular to the centrifugal direction and around 0.25 W/(m·K) in the out-of-plane direction. The anisotropy factor was about 1–2 in the in-plane thermal conductivity. The out-of-plane thermal conductivity was one order of magnitude lower than the in-plane thermal conductivity. The high thermal conductivity of P3HT films was also confirmed by Xu et al. (2018). They prepared a P3HT film using the bottom-up oxidative chemical vapor deposition method. Through engineering noncovalent inter-molecular interactions, they achieved an overall thermal conductivity of 2.2 W/(m·K) at near-room temperature; however, the anisotropic thermal behavior was not reported in their work.

Given the important effect of the stress/strain and special limitation on the polymer crystallization, electrospinning can effectively produce extremely narrow fibers from polymer solvent or melt with diameters ranging from a few nanometers to several micrometers (Yuan et al., 2017). The electrospinning system is composed of a high-voltage system, spinneret, and collector (Long et al., 2019). Ma et al. (2015) reported high thermal conductivity up to 9.3 W/(m·K) in a single PE nanofiber, which was 20 times the enhancement compared with the typical bulk value. The PE nanofiber was produced from PE/P-xylene solution using a 45 kV electrospinning voltage and a 150 mm needle/collector distance (Ma et al., 2015). The high thermal conductivity was due to highly oriented molecular chains caused by the strong stress and the enhanced crystallinity in the limited space in the thin nanofibers. Wang et al. (2009) confined the thickness of
a PEO film to 20 nm using an innovative layer-multiplying co-extrusion process, and confirmed the single, high-aspect-ratio lamellae crystalline structure in this film.

The orientation of crystallites in a product is also important in improving thermal conductivity. Randomly distributed crystallites will contribute little to improvements in thermal conductivity. Since stress can force a polymer to crystallize, hot stretching is a good post-process that is used to further improve the structure and thermal conductivity of fiber and film products. In a typical hot-stretching process, the polymer will be heated above its glass transient temperature \(T_g\) and then stretched. This process causes tangled molecular chains to move at the glass transient temperature, while the chains in crystallites do not. Since the sample’s cross section decreases during stretching, the crystallites automatically orient themselves to the stretching direction and form good alignment in the polymer. Shen et al. (2010) fabricated high-quality ultra-drawn PE nanofibers, in which the thermal conductivity reached as high as 104 W/(m·K)—about 400-fold enhancement compared with the bulk value of around 0.3–0.5 W/(m·K). The nanofibers were prepared using a two-stage heating method. They were drawn from a heated PE gel by using an atomic force microscope (AFM) cantilever and achieved diameters of 50–500 nm. Then, mechanical stretching was applied to the nanofibers. The highest thermal conductivity was achieved

![FIG. 4: Thermal conductivities (a) and thermal diffusivities (b) in three dimensions against the density for all P3HT thin films [reprinted with permission from Feng et al. (2013); © Elsevier]
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at a draw ratio of around 400. Compared with the mechanism of thermal conductivity enhancement in hot-stretching microfibers due to alignment of crystallites in the fiber, the low defects and forced alignment of molecular chains contributed to the improved quality toward the limit of a single crystal and thus the high thermal conductivity. The single crystal structure was confirmed by transmission electron microscopy in their work.

In previous theoretical studies, the single chain of the backbone has shown a stronger capability of conducting heat than the crystalline structure in polymers. A straightened molecular chain in the amorphous area will also contribute to an increase in thermal conductivity in polymers. Take polyethylene as an example, which has a simple structure containing only backbone chains. Zhu et al. (2017) carefully stretched ultra-high molecular weight (UHMW)-PE microfibers at an elevated temperature of 131.5°C, which is near the melting point, and at a very low strain rate of 0.0129 s\(^{-1}\). They obtained a high thermal conductivity of 50.8 W/(m·K) at a low strain ratio of 6.6, which was more than twice that of the \(k\) value of the original fiber [21 W/(m·K)]. Structure investigations, including X-ray diffraction (XRD), XRD pole figures, and polarized Raman spectroscopy, applied to this microfiber demonstrated that the crystallinity of the UHMW-PE microfibers decreased during stretching. The molecular chains in the amorphous region, instead of the crystallites, were better aligned along the stretching/axial directions and the local high thermal conductivity of the molecular chain greatly contributed to the enhancement of the overall thermal conductivity in this microfiber. This was the first time that the very high thermal conductivity of a PE microfiber was achieved by reducing the crystallinity, which directly confirmed the contribution of an amorphous alignment to an increase in the \(k\) value. Subsequently, this mechanism and structure were confirmed by Xu et al. (2019). However, the elevated temperature selection and controlling the hot stretching had significant effects on the final product, which varied from sample to sample.

The cold drawing process can also help align the orientation of crystallites in a fiber. Polymeric fibers and strips are stretched at room temperature in the cold drawing process. The crystallites will orient along the deformation direction according to the stress and strain. Nitta and Nomura (2014) investigated the tensile behavior of cold-drawn isotactic PPs. Their results showed that fragmented lamellar clusters were first aligned tightly in the necking region; the further elongation in the post-necking region was caused by the amorphous region between the crystalline lamellae, causing subsequent strain hardening to occur. Xiao et al. (2010) cold stretched a polyaniline film at room temperature at different strain levels. They found that the molecular chains and crystallites were forced to align along the stretching direction. In addition, the alignment of the molecular chain decreased the intermolecular distance and thus increased the crystallinity in the film. Cold stretching was found to be more efficient than hot stretching in increasing crystallinity.

### 3.2 Structure Characterization to Uncover Effects on Thermal Conductivity Improvement

After structure tailoring, it is critical to investigate the crystallinity, crystallite orientation, and other structure characteristics. XRD, XRD pole figures, and polarized Raman spectroscopy are preferable tools for this characterization. XRD is a well-known technique for structure characterization including crystal orientation, grain size, crystal defects, etc. (Kohli, 2012). Its mechanism can be simply described as follows: monochromatic X-rays are elastically scattered by atoms in a periodic lattice, and constructive interference occurs in the scatterings indicating the structure parameters of the periodic lattice. In Zhu et al. (2017), the XRD pattern of UHMW-PE fiber
bundles (Fig. 5) showed multiple diffraction peaks in the PE fiber bundle. Each diffraction peak position can be used to calculate the unit cell lattice parameters and the peak widths may denote the crystallite size, lattice strain, and defects. After heat stretching the UHMW-PE fiber bundles, no obvious difference in XRD patterns arises. This indicates that the crystalline structure does not degrade much and contributes to the elongation of MFP of phonons in the PE fiber.

In a regular XRD, the incident X-ray and detector for diffraction are paired to scan the diffraction due to the crystal structure and to determine the size of the crystalline size. However, to further investigate the orientation of crystals in a fiber, XRD pole figures will fix the incident X-ray and the detector, and rotate the sample to investigate variations of the diffraction along the rotating angle. Zhu et al. (2017) used pole figure patterns of the (002) plane of UHMW-PE to clarify the fact that no obvious enhancement occurred in the crystal orientation. As shown in Fig. 6, the XRD pole figure patterns of the same UHMW-PE fiber were almost the same before and after the stretching process. This result is consistent with the aforementioned XRD pattern study. Thus, Zhu et al. (2017) concluded that the alignment of the amorphous region can significantly improve the overall thermal conductivity rather than the crystal region in fibers of high crystallinity.

In addition to XRD technology, polarized Raman spectroscopy can detect the molecular orientation as well as provide the chemical bonds and structure information. In polarized Raman

![Fig. 5: XRD patterns of the UHMW-PE fiber bundles: the patterns before and after stretching do not show obvious differences, illustrating conservation of the original crystalline structure [reprinted with permission from Zhu et al. (2017); © American Chemical Society]](image-url)
Thermal Conductivity Enhancement of Polymers

FIG. 6: XRD pole figures of the (002) plane of the stretched (a) and reference (b) samples shows no significant difference; (c) schematic of the XRD pole figures; (d) intensity variation by varying the value of $\beta$ [reprinted with permission from Zhu et al. (2017); © American Chemical Society]

spectroscopy, the intensity of the scatterings depends on the polarization of incidence. The scatterings result from the interference of the polarized electromagnetic field of the incidence with vibrating molecules, which is direction sensitive (Jones et al., 2019). When the vibration direction is the same, the fluctuations in the polarizabilities of molecular vibrations can be detected and a corresponding Raman peak appears in the Raman spectrum. Variations in polarizabilities do not occur since the molecular vibration direction is perpendicular to the incident electromagnetic field. Zhu et al. (2017) used polarized Raman spectroscopy to measure the direction of the crystallites in UHMW-PE fiber before and after stretching. The results are shown in Fig. 7. The polarization direction was rotated between the axis direction of the fiber and the laser polarization, as denoted in by angle $\gamma$ Fig. 7. As the laser polarization was rotated from 0° to 90°, the crystalline band of 1416 cm$^{-1}$ became weaker but the amorphous bands at 1440 and 1460 cm$^{-1}$ obviously increased. The comparison between the normalized intensity of the polarized Raman spectroscopy results from the polymers before and after stretching in Figs. 7(b) and 7(c) illustrates the increments in the amorphous phase and their alignment.

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4. THERMAL CONDUCTIVITY MEASUREMENT: A CRITICAL ASPECT

4.1 Techniques for Thermal Characterization: A General Picture

It is well known that measuring the thermal properties is critical in order to deeply understand the thermal properties of polymers under structure tailoring. The methods used to measure the...
Thermal conductivity enhancement of polymers include the time-domain thermo-reflectance (TDTR) method (Wang et al., 2013), microfabricated bridge method (Li et al., 2003), pulsed photo-thermal radiometry (PPTR) method (Choy et al., 1997, 1999), bi-material AFM cantilever method (Shen et al., 2010), and transient electro-thermal (TET) technique. (Guo et al., 2007a).

As shown in Fig. 8(a), the TDTR method depends on the principle that a change in the reflecting probe beam intensity is proportional to the temperature change in the metal transducer. The known quantities in the analysis are the heat capacity and thickness of each layer (Cahill et al., 2002, 2003; Oyake et al., 2015). The sensitivities of the fitting signal to the thermal conductivity and the thickness are important in analyzing the uncertainties and error propagation. In a typical case, 5% uncertainty in thickness can lead to 10% uncertainty in the thermal conductivity, which means that attention should be paid to the thickness of each layer in order to ensure accurate measurements. The advantage of the TDTR method is that it does not require any resistance/temperature calibration. It is similar to the photo-thermal technique (Chen et al., 2010; Guo et al., 2009; Wang et al., 2008; Xu and Wang, 2014; Xu et al., 2014b), which operates in the frequency domain, but the TDTR method works in the time domain. The TDTR method has been proven to be a robust and routine method used to measure the thermal conductivity of ultra-thin films and interface thermal conductance.

For the microfabricated bridge method, the to-be-measured wire serves as a thermal bridge between two heater pads. These two heater pads also serve as a resistance thermometer to sense the temperature of each island. By solving the heat transfer equations of the system, the thermal conductivity of the wire can be obtained (Li et al., 2003). It should be noted that more attention should be paid to the thermal contact between the wire and suspended devices when doing this experiment. The microfabricated bridge method can measure the thermal property of nanoscale wires, while the fabrication of microdevices is complicated and time consuming. The PPTR method employs a line-shaped laser beam flushing on the surface of the sample at one side. At the same time, the temperature evolution at a distance from the line source is monitored by an infrared (IR) method. By fitting the radiometry signal, the in-plane thermal diffusivity of the measured sample can be determined (Choy et al., 1997). The limitations of the PPTR method occur when samples have low IR emissivity or low laser-damage thresholds. An experimental schematic illustration of the PPTR method is shown in Fig. 8(b).

![Schematic diagrams of the experimental setups for the TDTR method (a) [reprinted with permission from Cahill (2018); © Materials Research Society] and the PPTR method (b) [reprinted with permission from Choy et al. (1997); © John Wiley & Sons]](image-url)
The bi-material AFM cantilever method for micro/nanofibers was developed in Chen’s group; a detailed description of the experimental setup can be found in Shen et al. (2010). The sample was bridged between a thermocouple and an AFM cantilever. The thermocouple was mounted on the tip of a steel needle and was heated by the needle to a desired temperature, while the cantilever was bi-material and its deflection was very sensitive to power/energy variations. A laser beam was focused on the cantilever to record the deflection of the cantilever and the power variations due to temperature changes by using a photodiode. According to the minute changes in the conducted heat against the temperature variation of the thermocouple, the thermal conductivity of the sample was determined. The aforementioned methods all have their own advantages and disadvantages.

4.2 TET and Pulsed Laser-Assisted Thermal Relaxation Techniques: High Accuracy and Ease of Operation

Compared with the TDTR and microfabricated bridge methods, the TET technique developed by Wang’s group at Iowa State University is ready to build, and no calibration is required to measure the thermal diffusivity. Figure 9 shows a schematic of the TET and pulsed laser-assisted thermal relaxation 2 (PLTR2) techniques. In the TET experiment, the to-be-measured sample is suspended between two electrodes. The entire sample is placed in a vacuum chamber in order to eliminate thermal convection. Since polymer is non-conductive, it should be coated first with gold or another metal (approximately of nanometer thickness) before the test. During the test, a direct current (DC) is fed to the sample to induce joule heating in the metal film, which also transports the heat to the sample. The evolution of voltage over the sample is recorded by an oscilloscope to indicate the temperature evolution of the sample. Based on the experiment, the normalized temperature rise can be calculated from the observed voltage change \( V \) of the sample over time as

\[
T^* = \frac{V - V_0}{V_\infty - V_0},
\]

where \( V_0 \) and \( V_\infty \) are the voltage of the sample before and after heating, respectively. Once the normalized temperature evolution is obtained, the thermal diffusivity of the sample can be obtained by fitting the normalized temperature change curve against time. The heat conduction along the fiber can be treated as one-dimensional due to the sample’s high length-to-diameter ratio. The governing equation is

\[
\frac{\partial (\rho c_p T)}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \dot{q}
\]

where \( \rho, c_p, \) and \( k \) are the density, specific heat, and thermal conductivity of the sample, respectively. Here, \( \dot{q} = I^2 R_s / AL \), where \( A \) and \( L \) are the cross-sectional area and length of the sample, respectively. The boundary and initial conditions are \( T(x = 0, x = L) = T_0 \) and \( T(t = 0) = T_0 \), respectively. The theoretical normalized temperature rise, which is defined as

\[
T^*(t) = \frac{T(t) - T_0}{T(t \to \infty) - T_0},
\]

is solved as follows (Guo et al., 2007b):

\[
T^* = \frac{96}{\pi^4} \sum_{m=1}^{\infty} \frac{1 - \exp \left[ - \frac{(2m - 1)^2 \pi^2 \alpha_{\text{eff}} t}{L^2} \right]}{(2m - 1)^4}
\]

where \( \alpha_{\text{eff}} \) is the sample’s effective thermal diffusivity, which includes the effect of radiation and metal coating. During the fitting, the theoretical normalized temperature rise is calculated according to Eq. (3) by using different trial values of \( \alpha_{\text{eff}} \), and the calculations are then compared with the experimental results. The trial value that gives the best fit of the experiment data is taken.
FIG. 9: Schematic diagrams of the experimental and physical principles of the TET and PLTR2 techniques [reprinted with permission from Feng et al. (2013); © Elsevier]

as the sample’s effective thermal diffusivity ($\alpha_{\text{eff}}$). The real thermal diffusivity of the sample can be obtained by subtracting the effect of the radiation and gold coating; the details of which can be found in Guo et al. (2007b) and Liu et al. (2014, 2015).
The TET technique is mostly applied to analyze the in-plane thermal transport. Wang’s laboratory also developed the PLTR2 technique to investigate the cross-plane thermal transport (see Feng et al., 2013). The original pulsed laser-assisted thermal relaxation technique was also developed by Wang’s laboratory, which used a nanosecond pulsed laser to heat up a suspended sample and observe the temperature/voltage relaxation of the sample in order to determine its thermal diffusivity (see Guo et al., 2008). An experimental schematic illustration of the PLTR2 technique is shown in Fig. 9. Before the test, the two sides of a P3HT film were coated with gold. Then, the sample was bridged between two electrodes. Silver paste was used to ensure low thermal resistance between the sample and the electrodes. It should be noted that the topside gold film was not in contact with the electrodes. During the experiment, a nanosecond pulsed laser with a 1064-nm wavelength irradiated the top side of the sample. The wavelength of the pulsed laser did not need to be 1064 nm as long as the gold film had high absorption at a certain wavelength. At the same time, a constant DC was fed through the gold film on the bottom to sense the temperature change. This DC was carefully selected to ensure both perceptible voltage changes and minimum joule heating. The voltage evolution of the bottom-side gold film was monitored by an oscilloscope.

In the PLTR2 measurement setup, the gold film on the top absorbs the laser energy and then its temperature begins to rise. Since the topside gold film is not in contact with the electrodes, the thermal energy is transferred from the topside gold film to the P3HT film. This cross-plane thermal transport has been proven to be extremely fast, i.e., on the order of hundreds of microseconds (Feng et al., 2013). The cross-plane thermal diffusivity is derived as follows: \( \alpha = \frac{1.38D^2}{\pi^2} \times \frac{1}{t_{1/2}} \) (Parker et al., 1961), where \( D \) is the thickness of the P3HT film and \( t_{1/2} \) is the time taken to reach one-half of the maximum temperature rise. As shown in Fig. 9, the very fast cross-plane thermal transport part is followed by in-plane thermal transport due to the heat dissipation from the P3HT film to the electrodes. Since time is in the temperature decay region, due to the very high length-to-thickness ratio, the thermal transport can be simplified as one-dimensional along the length direction. The governing equation is (Feng et al., 2013):

\[
\frac{\partial (\rho c_p T)}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + q_0, \quad \begin{cases} q_{\text{laser}} + q_{\text{joule}}, & 0 \leq t \leq \Delta t \\ q_{\text{joule}}, & t > \Delta t \end{cases}
\]

(4)

where \( \Delta t \) is the laser pulse width (\( \sim 7 \) ns). Here, \( q_0 \) includes both the laser beam energy and the joule heating since \( t \) is smaller than \( \Delta t \). Two simplifications were applied to solve the previous equation based on the following facts: (1) the joule heating was relatively weaker than the laser energy; therefore, only the laser pulsed energy was considered in the following analysis; (2) a laser beam spot larger than the sample size was chosen to ensure uniform laser energy irradiating on the film. The normalized temperature for the thermal decay process is

\[
T' = \frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{\exp \left[ -\frac{(2m-1)^2 \pi^2 \alpha t}{L^2} \right]}{(2m-1)^2} \]

(5)

After obtaining the normalized temperature profile from the experimental data, different values of the thermal diffusivity (in-plane) were tried to fit the normalized temperature. The value giving the best fit was taken as the in-plane thermal diffusivity of the P3HT film. The TET and PLTR2 techniques have been evaluated rigorously with sound accuracy and high reliability in Wang’s laboratory to characterize the thermal properties of various conductive and non-conductive micro/nanoscale fibers/films (Feng et al., 2013; Liu et al., 2015, 2016; Xie et al., 2015).
Although thermal characterization seems straightforward, great care has to be taken in experimental design and data analysis. In the past, the thermal conductivity of many polymers was incorrectly claimed due to ignored or mistreated radiation effects, which become dominant when wire/film-like samples have very high-aspect ratios. Examples of the radiation effect being given rigorous consideration can be found in the studies conducted by Wang’s group (see Xie et al., 2016). Also, heating rate evaluations and temperature measurements can become very challenging using techniques that rely on direct knowledge of the heating rate and temperature rise for direct thermal conductivity calculations. The TET and PLTR2 techniques only probe the relative evolution of the temperature rise of samples, and they do not need the heating rate and absolute temperature information. They have been proven to give some of the best accuracy measurements for fiber-like and film-like samples (Guo et al., 2007a; Han et al., 2018) and are far superior to the \( 3\omega \) technique (Choi et al., 2006).

### 4.3 Structure Analysis based on Phonon Scattering: Thermal Reffusivity

It has been commonly recognized that thermal conductivity strongly depends on the micro/nano-scale structure of materials. However, if only the \( k-T \) profile of materials is examined, very little information regarding the microstructure can be obtained. Based on a phonon scattering mechanism, a new physical term called thermal reffusivity has been proposed to characterize the structural size of various materials. It was first proposed by Xu et al. (2014a) to study the structure size in DNA. Then, it was developed and proved applicable in various materials such as polymers and carbon-based materials (Liu et al., 2015, 2017; Xie et al., 2015, 2018b). In this section, we focus on applying the thermal reffusivity theory to polymers in order to improve the structural size.

In non-metal materials, phonons are the major heat carriers. The thermal resistance arises from phonon scattering. There are two types of phonon scattering: phonon–phonon scattering and phonon–defect scattering. Chemical impurities, grain boundaries, lattice defects, and rough edges are the common defects. Phonon–phonon scattering is proportional to the phonon population and dependent on temperature. As the temperature decreases, due to the largely reduced phonon population, phonon–phonon scattering becomes weak while the phonon–defect scattering becomes dominant.

For isotropic and non-metallic materials, the thermal reffusivity (\( \Theta \)) is defined as follows: \( \Theta = 1/\alpha \). Here, \( \alpha \) is the thermal diffusivity. According to Matthiessen’s rule, and taking into consideration different scattering mechanisms, the combined relaxation time (\( \tau_c \)) can be written as follows:

\[
\frac{1}{\tau_c} = \frac{1}{\tau_{\text{ph-ph}}} + \frac{1}{\tau_{\text{imp}}} + \frac{1}{\tau_{\text{GB}}} + \frac{1}{\tau_{\text{surf}}} \tag{6}
\]

where \( \text{ph-ph} \), imp, GB, and surf indicate phonon–phonon, phonon–impurity, phonon–grain boundary, and phonon–surface scattering, respectively. Combining Eq. (6) with the definition of thermal reffusivity, the equation for \( \Theta \) can be written as follows:

\[
\Theta = \frac{3}{v^2} \left( \frac{1}{\tau_{\text{ph-ph}}} + \frac{1}{\tau_{\text{imp}}} + \frac{1}{\tau_{\text{GB}}} + \frac{1}{\tau_{\text{surf}}} \right) \tag{7}
\]

where \( v \) is the phonon velocity. Equation (7) can be rewritten as \( \Theta = \Theta_{\text{ph-ph}} + \Theta_0 \) if we regard all of the impurities, grain boundaries, and surfaces as the defects, where \( \Theta_0 \) is the thermal reffusivity due to phonon–defect scattering, and \( \Theta_{\text{ph-ph}} \) is the thermal reffusivity due to phonon–phonon scattering. As the temperature decreases to 0 K, phonon–phonon scattering vanishes, and
residual thermal reffusivity appears due to phonon–defect scattering. If there are rare chemical impurities and lattice defects in the materials, then phonon–grain boundary scattering dominates at 0 K; namely, \( \Theta_0 = \frac{3}{(vl)} \), where \( l \) is the MFP due to phonon–grain boundary scattering, which is proportional to the average grain size (or very close to it). It can be clearly seen that the residual thermal reffusivity is directly related to the grain size; the larger the grain size, the smaller is the value of \( \Theta_0 \).

The thermal reffusivity theory can be applied to study the grain size of materials. Since the \( \Theta_0 \) values of carbon nanocoils were obtained from the experiments, the grain sizes were calculated using Eq. (7). The thermal reffusivities of the carbon nanocoils, graphite, and graphene foam are shown in Figs. 10(a)–10(c), respectively. Deng et al. (2016) analyzed the grain sizes of carbon nanocoils by using the thermal reffusivity theory, Raman method, and XRD. It was found that the grain sizes obtained by the thermal reffusivity theory agreed well with the values obtained from Raman spectra and XRD (Deng et al., 2016).

The thermal reffusivity theory can also be used to investigate mechanisms that can improve the thermal properties of stretched PE fibers. Zhu et al. (2017) studied the thermal properties and grain sizes of UHMW-PE fibers under hot stretching. Figure 11 shows the thermal reffusivities of the stretched and reference PE fibers, where it is observed that the residual thermal reffusivities of the stretched PE fibers have decreased compared with their corresponding reference fibers. This indicates that the grain sizes increased after being stretched, which was verified by XRD (Zhu et al., 2017). In addition, the fitting curves of the stretched PE fibers changed more smoothly with the changes in temperature than did those of the reference fibers due to the Debye

FIG. 10: Thermal reffusivity of carbon nanocoils (a), graphite (b), and graphene foam (c) at different temperatures [reprinted with permission from Deng et al. (2016); © American Chemical Society]
FIG. 11: Changes in the value of $\Theta$ with temperature for samples A, B, and C. $\Theta_0$ is fitted from fourth-order polynomial regression [reprinted with permission from Zhu et al. (2017); © American Chemical Society]

temperature decreasing after the PE fibers were hot stretched (Xie et al., 2015). Further structure analysis indicated that the increase in the thermal diffusivity in the stretched samples was a result of the better alignment of the amorphous part in the PE fibers (Zhu et al., 2017).

In this work, it was found that the thermal reffusivity successfully evaluated the structural improvements of hot-stretched PE fibers. The thermal reffusivity theory is not only applicable to polymers, it has also been successfully applied to quantitative analyses of the structural size and Debye temperature of carbon-based materials such as graphene paper (Xie et al., 2015, 2018b)
and carbon fiber (Liu et al., 2017). In addition to semi-crystalline materials, the thermal refusivity theory can also successfully evaluate the structural domain size of Asian human hair. This indicates thermal refusivity is a powerful tool that can be used to analyze the structure of amorphous materials (Xie et al., 2018b); however, this important role of thermal refusivity in analyzing the microstructure of various materials has been overlooked by researchers in previous works. Due to the ultrathin scattering cross section in two-dimensional materials, such as graphene and MoS$_2$, it is hard to directly obtain information about the in-plane structure using traditional beam scattering methods, such as XRD. Instead, thermal refusivity near 0 K provides a very promising tool that can be used to characterize the in-plane structure domain size.

5. CONCLUDING REMARKS

The thermal conductivity of polymers is significantly determined by its crystallinity, grain alignment, crystal grain size, and amorphous regions connecting the crystallites. To understand the mechanism of improving the thermal conductivity, four fundamental physics principles have been summarized in this review. Methods for fabricating and structure tailoring, including compression molding, injection molding, electrospinning, and stretching and coating methods were reviewed based on these four principles. Additionally, some widely used thermal probing techniques (the TET and PLRT2 techniques) were also reviewed for multi-dimensional thermal probing at the micro/nanoscale. The TET and PLRT2 techniques provide some of the best accuracy measurements of the thermal conductivity of polymers in the form of wire and films.

Although a crystalline structure is preferred for achieving high thermal conductivity of polymers, the high crystallinity will reduce the flexibility of the polymers, which makes the polymeric products brittle. Utilizing the alignment of molecular chains along the desired directions in amorphous regions provide great potential for enhancing the thermal conductivity without significantly sacrificing the mechanical properties. Understanding the detailed mechanisms involved in heat conduction by polymer chains remains a challenge, and more effort is needed to explore and even control these mechanisms. Furthermore, there are numerous challenges that need to be resolved before industries can proceed with the mass production of structure-tailored polymers with high thermal conductivity. The current structure tailoring of polymers has been limited to thin films or micro/nanofibers. This significantly limits their application. It is critical to tailor the structure of bulk polymers (three-dimensional) toward broader applications. To better control the thermal performance of fabricated polymers, novel thermal measurement techniques are still highly in demand, which could flexibly fit in the in situ measurement of different structures at small scales.

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