Thermal Conductivity Enhancement of Polymers via Structure Tailoring

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Abstract

Polymers are usually known for its low thermal conductivity. However, high thermal conductive polymers are in growing demand in industry nowadays for 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 the thermal conductivity \(k\) but it is clearly noticed 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 perspectives of polymer intrinsic structure tailoring: crystallinity, orientation of crystallites, crystalline grain size, and the alignment of molecular chain in amorphous region. Structure tailoring methods of increasing/improving those four factors are critically reviewed and discussed. Accurate thermal characterization methods are critically reviewed for those structure-tailored polymers in low dimensions. The transient electro-thermal (TET) and pulsed laser-assisted thermal

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relaxation 2 (PLTR2) techniques provide some of the best accuracy thermal conductivity measurement with high physics control.

**Keywords:** Structure Tailoring, Thermal characterization, Polymers, Thermal conductivity
Catalog

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1. Introduction

1.1 High demand of polymers of high-thermal conductivities

Polymers are preferable in current industry for their low cost, flexibility, and good environmental resistance, etc., but most of them are regarded as thermal isolation materials for their low thermal conductivity ($k$) is usually lower than 0.5 W/m·K[1]. For example, among major industrial polymers, the acrylic glass (Poly(methyl methacrylate), PMMA), an alternative optical material, has a $k$ of ~ 0.2 W/m·K. The low $k$ of other polymers, given a few examples, is 0.25 W/m·K for nylon and polyvinyl chloride (PVC) (a flame retardant material), 0.3–0.5 W/m·K for polyethylene (PE) that is frequently used in food industry, and 0.17–0.22 W/m·K for polypropylene (PP)[2]. 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 highly demanded in current industry in the field of electronic packaging in micro-electromechanical system (MEMS), especially when the electronic devices are keeping miniaturization in nowadays[3]. The high power density of the devices generates a large amount of heat in a small scale and demands efficient high heat dissipation rate. Meanwhile good electric isolation is needed to maintain devices’ good performance. Thus, high thermal conductivity polymers will be a potential candidate instead of metallic materials for the good thermal management purpose in miniaturized devices. Besides, 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[4, 5], though metallic materials are preferable in heat dissipations, their large mass, electrically conduction sometimes may not fit in the situation. In the
field of thermal protection[6], thermal protection on human body has the contradictory requirements of heat isolation and dissipation under the ergonomics and physiological considerations. It should block high temperature outside the protection suit and be capable of conduct heat and humidity toward outside from human body. Also, a low mass is expected for the suit. In this case, easily fabricated polymer with a controllable high thermal conductivity is a good candidate for thermal protection. Thus, the enhancement in thermal conductivity of polymers is urgently needed in these fields[7].

1.2 Thermal conductivity enhancement in polymer-based composites

In the past, researchers have made great efforts to increase the k of polymers through composition, such as embedding/dispersing high-k fillers in polymer base, including metallic particles[8, 9], ceramic particles[10-14], carbon nanotubes[15, 16], and graphene[17-19]. Chen et al. 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 8-fold higher than that of the plain epoxy resin[9]. To utilize the high thermal conductivity of ceramic particles, Kim et al. embedded boron nitride powder fillers into an epoxy-terminated dimethylsiloxane matrix[14]. The surface of boron nitride particles was hydroxyl-functionalized and doped with surface curing agents so that the ceramic particles could be chemically bonded with the epoxy resin. In this composite, the thermal conductivity was enhanced up to 70%. Carbon nanomaterials are preferable after they were discovered and as they exhibit desirable physical properties of low density and ultrahigh thermal conductivity. Biercuk et al. prepared single-walled carbon nanotube/epoxy composite with 1wt% unpurified carbon nanotube load and found a 125% increase in the thermal conductivity at room temperature[20]. Song et al. bonded graphene flakes to 1-pyrenebutyric acid (PBA) through π-π
stacking and added this nanocomposite into epoxy resin to increase the overall thermal conductivity of the resin to 1.53 W/m·K[17]. The mechanisms of controllable enhancement of thermal conductivity in polymer-based composites, including filler loads, morphology of fillers, interface between fillers and bases, either with or without the inter-filler networks, have been widely discussed and summarized in some comprehensive review works[21, 22].

Adding high-$k$ fillers has been widely proved an efficient way to control and optimize the thermal conductivity of composites systems over pure polymer systems. But in literatures, for most crystalline or semi-crystalline polymers, increasing the quantity of fillers will decrease their overall mechanical performance[23]. Furthermore, when one-dimensional size of polymers goes from macro- to micro/nano-scale, the fillers will largely decrease the strength in mechanical behavior of polymers, especially the strength. Therefore, it significantly limits the application of fillers at the small scale. A more workable approach is to improve the $k$ of polymers by tailoring their microscopic structure instead of using fillers. This review will focus on the physics and techniques for significantly improving the $k$ of polymers by tailoring their microscopic structures. The physics principles of structure tailoring are discussed in Sec. 2 and based on these principles, the commonly used methods for structure tailoring and structure characterization are summarized in Sec. 3. Section 4 presents the advanced and efficient technologies for thermal properties measurement of the enhanced polymers, especially for 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 polymers’ $k$ based on molecular dynamics (MD) simulation or other methods using a single molecular chain usually cannot consider all these structural effects. As a result, the reported $k$ sometimes even becomes divergent. Using the Green-Kubo approach and a modal decomposition method, Henry and Chen reported a $k$ of $\sim 350$ W/m·K for PE$[24]$. For PE polymer chains, a latter-on work by Liu and Yang pointed out that if there is no defect in the polymer chains, $k$ will keep increasing with the polymer length when phonon boundary scattering is lacking$[25]$. In that work, it reported the anomalous heat diffusion and $k$ increases with the polymer chain length $L_0$ as $k = CL_0^a$, where $C$ is 19.58, and $a = 0.382$, and $L_0$ in the unit of nm. Such anomalous heat diffusion was also found for other different polymer chains as shown in Fig. 1. It has been extensively studied and confirmed, and is termed anomalous heat diffusion$[26]$. Therefore, great caution should be exercised to report the intrinsic thermal conductivity of single polymer chain using MD simulations when no defect is present. The non-perfect structure of real polymer chains will significantly reduce its $k$. For instance, using MD simulation, Liu's group has uncovered that the kinks in PE's molecular chains could significantly reduce its $k$[27]. For each kink in the PE chain, a thermal resistance of $\sim 3.7 \times 10^{-10}$ m$^2$K/W arises. Therefore, the kink’s existence and their number of density can affect the overall thermal conductivity of the PE chain significantly. Despite some limitations in theoretical studies, they still provide great insight into the heat conduction in polymers which could help understand the experimental observations. Some cautions need to be taken when using theoretical predictions to predict the upper limit $k$ of polymer chains.
As will be detailed in section 4.3 for 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, thermal conductivity increase consideration should also consider the crystalline grain orientation and amorphous region alignment. To improve the $k$ of polymers, four fundamental physics principles are usually taken. The first one is to improve the crystallinity level of the material since the crystalline structure has a $k$ much higher than that of the amorphous region. At the room temperature, PE of 81% crystallinity was reported to have a $k$ 70% higher than that of 43% crystalline PE[28]. If a polymer has a high anisotropic structure (most cases it is true), the polymer chain direction will have a much higher $k$ than that in other directions. When talking about $k$ increase, here $k$ is referred to that in 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%, further crystallinity increase becomes more difficult and the corresponding $k$ increase becomes very marginal. In polymers, the 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 amorphous region in the material will reduce the overall thermal conductivity significantly. For instance, the extreme case would be an amorphous region connected with the crystalline part in serial in the polymer chain direction. If $k_a$ equals 0.01$k_c$, even when the amorphous region takes 10% volume, the overall $k$ will only be 0.092$k_c$. This clearly illustrates the limitation of $k$ increase by increasing the crystallinity. If the amorphous region is connected with the crystalline part in parallel, the overall $k$ will be 0.901$k_c$. For real situations, both parallel and serial connections co-exist[29]. So if a strategy is taken to increase the crystallinity level for $k$ improvement, it is best to reduce the amorphous region portion serially connected with the polymer chains. This serial and parallel connected structure analysis could also provide a quick theoretical estimate to check the validity of some 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 $k$ since the crystal has strong anisotropic nature of $k$. Aligning the high-$k$ direction of nanograins along the same direction is critical to achieve a very high effective $k$. This has been widely recognized when increasing $k$ of low-$k$ materials by dispersing some high-$k$ particles, flakes and rods. It is not only the $k$ of the material, but also their microscopic orientation that determines the overall $k$. In the work by Wang et al. on the $k$ of nanofluids, it was pointed out that nanoparticle chains/clusters will help improve the thermal conductivity of nanofluids more over that with just simply dispersed nanoparticles[30]. Latter-on such mechanism was observed and proved in the
work by Gao et al[31]. Therefore, for polymers, if the stretching/drawing cannot simply increase the crystallinity, but make the crystallites more aligned along the drawing direction, the final $k$ 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%, but the crystalline grains are randomly distributed within the material, the overall thermal conductivity ($k$) can be estimated using the Maxwell's equation as:

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

where $k_a$ is the amorphous region's thermal conductivity, $\alpha = k_c / k_a$, and $k_c$ is the effective thermal conductivity of the crystalline grains (considering its 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 grains is also aligned along the heat transfer direction, the situation will change very much. The polymer chain direction thermal conductivity ($k_{c2}$) usually is much higher than $k_a$. Here we take $k_{c2} = 20k_a$. Under such aligned situations, the thermal conductivity of the polymer will be $k = \phi k_{c2} + (1 - \phi)k_a = 2.9k_a$. 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 $k$. This is because if the grain has a small size (e.g. a few nm), the phonon mean free path (along the chain direction) will be significantly limited by the grain size and boundary scattering, thereby reducing the thermal conductivity of the grain significantly. Such size effect, by the first order, can be expressed as $l^{-1} = l_0^{-1} + l_g^{-1}$, where $l$ is the phonon mean free path (MFP) in the crystalline grain, $l_0$ is the intrinsic MFP of phonons and $l_g$ the characteristic length of the grain. It needs to point out
that for a nanograin of a polymer, the grain size in the direction parallel to the polymer chain and normal to the polymer chain both will affect the $k$ in the chain direction[32, 33]. For polymers, the atomic bonding between atoms along the chain direction (intra-chain) is covalent, and could transfer energy very fast from atoms to atoms. The interaction between chains is via the Van de Waals force, and is usually much weaker. Therefore, it is expected the grain size in the direction normal to the polymer chain direction will have 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 ($k_{\text{eff}}$) is related to the grain size ($L$) in the chain direction as $k_{\text{eff}} / k_c = (1 + P \cdot l / L)^{-1}$, where $k_c$ is the thermal conductivity of defect-free infinitely large polymer crystal, and $l$ is the intrinsic mean free path[33]. Here $P$ is the correlation related to boundary conditions of the crystallite. For the size effect, Figure 2 illustrates how the thermal conductivity changes with the length for a graphene nanoribbon of 1.99 nm width[33]. Such 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.

Figure 2. Thermal diffusivity ($\alpha$) and thermal conductivity ($k$) variation against the graphene nanoribbon length. [Reprinted from Ref. [33]. Reproduced with permission of American Physical
The fourth principle is to align the amorphous polymer region, especially the region connected in serial with the crystalline part. This is different from the first principle discussed above which focuses only on increasing the crystallinity level. As there are always amorphous regions in a polymer material (the material cannot be 100% crystalline), the amorphous region connected with crystallites in serial 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.[29] as shown in Fig. 3. Since the polymer chains have intra-chain covalent bonds 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 crystallites to increase the overall $k$ significantly. In the above-mentioned theoretical work on the $k$ of PE, only a single molecular chain was studied. Therefore, its prediction can also be applied to the amorphous chain’s $k$. If an amorphous chain is not straight, the heat conduction along it will go through a relatively much longer path, making the effective $k$ much lower. Such physics can also be used to explain the very low thermal conductivity/diffusivity of carbon nanotube bundles[34] and graphene foams[35]. As mentioned above, the amorphous region connected in serial with the crystallite in the polymer chain direction plays a critical part in determining the overall thermal conductivity. Therefore, aligning the amorphous in this region makes the most sense in increasing the thermal conductivity. Some of the work reporting significantly increased $k$ of polymers upon drawing/stretching clearly confirms this amorphous alignment mechanism[36, 37].
Figure 3. Schematic to illustrate the amorphous region alignment effect on the thermal conductivity of PE fiber. (a) Amorphous region alignment after stretching, $\phi_{a,\perp}$, $\phi_{a,//}$, and $\phi_c$ denote the volumetric fraction of serial amorphous regions, parallel amorphous regions and crystalline regions respectively. (b) A simplified thermal resistance network model to quantify the effect of various regions. $R_{a,\perp}$, $R_{a,//}$ and $R_c$ are the thermal resistances of serial amorphous region, parallel amorphous region and crystalline region. For a sample of unit length and cross-sectional area, 

$$R_{a,\perp} = \phi_{a,\perp} / [k_a (\phi_{a,\perp} + \phi_c)^2]$$

$$R_{a,//} = 1 / k_a \phi_{a,//}$$

$$R_c = \phi_c / [k_a (\phi_{a,\perp} + \phi_c)^2]$$

and

$$1 / R_{eff} = 1 / R_{a,//} + 1 / (R_{a,\perp} + R_c).$$

(c) Thermal conductivity variation against the fraction of serially connected amorphous region to explain why the thermal conductivity increases when the crystallinity is reduced. [Reprinted from Ref. [29]. Copyright (2017) American Chemical Society]
For $k$ increase, the intrinsic structure of the polymer itself also plays a critical role. Take PE as an example, the length of the molecular chain has direct impact on the thermal conductivity. Short polymer chains tend to form small crystallites or crystallites with many dangling chain segments. The former one reduces the $k$ of the crystalline region because of the short mean free path, and the latter one will introduce more defects inside the crystallite, and on the crystallites’ boundary and limit the heat conductance. The longer molecular chains, however, the fewer dangling chain segments and thus fewer defects on the boundary. Besides, some polymer chain may be long enough that both of its ends engaged in crystallites, and its chain can conduct heat more efficiently than tangled tails of different chains. For polymers, the structure of the monomer itself is also critical for the thermal conductivity. A general rule is that if the monomers have more branched/complicated structures (e.g. like higher order randomness), the overall thermal conductivity tends to be lower[38, 39]. This is because that the existence of the branched structures will occupy the space between backbone chains and hinders the interaction between backbone chains including the formation of the crystallites[40]. This explains why PE has the highest thermal conductivity in reported polymers. For copolymers, the junction of the chains makes the overall structure tend to be much less perfect, leading to a much lower thermal conductivity[41-43]. This is because first of all, the junction will cause significant local phonon scattering and reduce the thermal conductivity along the chain direction. Second the junction itself makes it much less possible to form single crystalline grains in the material.

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

3. Methods for Structure Tailoring

3.1. Structure tailoring

Based on the abovementioned four mechanisms, tailoring 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 the solidification from polymer melt. When the temperature is above the melting point, all 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 rest 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. It directly compresses the melt into a desired shape and releases the resulted bulk after it is cooled. The cooling process is critical in crystallite growth. Theoretically, the longer the cooling process lasts, the larger the crystallites are obtained[44]. However, the long cooling period is not practiced in industry. Another popular technique for fiber and film fabrication is injection
molding. In this process, the molten polymer passes through a nozzle which 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 resulted fibers and films. Temperature and flow rate controlling are key factors affecting the crystallinity of the resulted products.

Nucleating agents could increase crystalline growth rate and ease the polymer crystallization[45]. They function as nuclei in polymer solution or melt which interact with polymer’s molecules to start the polymer nucleation. They could be low molecular weight crystalline particles, crystalline polymers, and metal salts of organic acids which are crystalline at the melting point of polymers, etc. Applying nucleating agents could increase the crystallinity of polymers, however, the suitable nucleating agents for polymers vary from one type to another, and is empirical to some extent. The development and dispersion of the nucleation agents still face big concerns in industry.

Coating and deposition processes employ the substrate as the nucleating agent. Li et al.[46] have reviewed the effect of surface on epitaxial crystallization of polymers. On a flat surface, the crystalline substrate surface will restrict the crystalline orientation and structure in grown polymer film when the crystalline polymer structure matches the substrate’s structure. Peculiar interaction is important for polymer crystallization on an amorphous structure. For curved surfaces, like a fiber surface, the intrinsic surface characteristics, interface stress, and flow field should be taken into account in generating polymer crystallization. Wang et al. investigated the semi-crystalline polymer thin films prepared by the physical vapor deposition (PVD) method, and controlled film morphology and thermal properties of MAPLE-deposited polyethylene oxide (PEO) films by
tuning the temperature and type of the substrates[47]. Confining environments are widely used to generate homogeneous nucleation in polymers[48, 49]. Li et al. spin-coated P3HT film on a nanostructured pattern[50]. Small amount of dissolved photoresist in 1,5-pentanediol offered nucleating agents and the nanopattern confined the crystalline growth direction. Both of them achieved directional organic crystal fibers of 2 μm wide and centimeters long.

The spin-coating fabrication process could align the molecular structures along the centrifugal direction to yield highly anisotropic mechanical and thermal properties of polymers. Feng et al. fabricated highly anisotropic thin poly(3-hexylthiophene) (P3HT) film using this technique[51]. In their work, regioregular P3HT was first dissolved in the chloroform solvent, and spin-coated on a glass plate with a high speed of 5000 rpm. The thickness of the P3HT films ranged from 20 to 40 μm. Different concentrations of the solution caused the different densities of the films in the spinning-coating process. Based on these samples, the advanced thermal measurement revealed the trend that 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[52]. The produced P3HT film had strong anisotropic structure and thus the thermal properties in the film. The thermal measurement result is shown in Fig. 4. The $k$ up to 3.18 W/m·K occurred along the centrifugal direction. The $k$ was around 0.6 W/m·K in the in-plane direction perpendicular to the centrifugal direction and was 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 ones. The high thermal conductivity of P3HT films was also confirmed by Xu’s work[53]. They prepared the 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 the near-room temperature, but the anisotropic thermal behavior was not reported in this work.

![Graph showing thermal conductivities and diffusivities against density](image)

Figure 4. (a) Thermal conductivities (a) and thermal diffusivities (b) in three dimensions against density for all P3HT thin films. [Reprinted from Ref.[52], Copyright (2013), with permission of Elsevier].

Given the important effect of stress/strain and special limitation on the polymer crystallization, electrospinning could effectively produce extremely narrow fiber from polymer solvent or melt with diameters ranging from a few nanometers to several micrometers[54]. The electrospinning system is composed of a high-voltage system, spinneret, and collector[55]. Ma et al. reported a
high thermal conductivity up to 9.3 W/m·K in a single PE nanofiber which was 20 times enhancement compared with the typical bulk value. It was produced from PE/ P-xylene solution using a 45 kV electrospinning voltage and a 150 mm needle-collector distance[56]. The high thermal conductivity is due to highly oriented molecular chains caused by the strong stress and the enhanced crystallinity in limited space in such thin nanofibers. Wang et al. confined the thickness of polyethylene oxide (PEO) film to 20 nm using an innovative layer-multiplying coextrusion process, and confirmed the single, high-aspect-ratio lamellae crystalline structure in this film[57].

The orientation of crystallites in the product is also important for $k$ improvement. Randomly distributed crystallites will contribute little to the $k$ improvement. As stress could force the polymer to crystallize, hot-stretching is a good post-process 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 is because the tangled molecular chains begin to move at $T_g$ while the ones in crystallites do not. As the sample's cross-section decreases during stretching, the crystallites will automatically orient to the stretching direction and form a good alignment in the polymer. Shen et al. fabricated the high-quality ultra-drawn polyethylene nanofibers whose thermal conductivity can reach as high as 104 W/m·K[58], about four-hundred-fold enhancement compared with its bulk value around 0.3~0.5 W/m·K. The nanofibers were prepared using a two-stage heating method. They were drawn from a heated polyethylene gel by using atomic force microscope cantilever and achieved 50-500 nm in diameter. Then the mechanically stretching was applied to the nanofibers. The highest thermal conductivity was achieved at the draw ratio around 400. Different from the mechanism of thermal conductivity enhancement in the hot-stretching microfibers due to alignment of crystallites in the fiber, the low
defects and forced alignment of molecular chains contributed to the quality improvement towards the limit of a single crystal and thus the high thermal conductivity. The single crystal structure was confirmed by TEM in their work.

In previous theoretical studies, the single chain of the backbone shows the stronger capability of conducting heat than the crystalline structure in polymers. The straightened molecular chain in the amorphous area will also contribute to the increase in the thermal conductivity of polymers. Take polyethylene (PE) as an example, it has a simple structure containing only backbone chains. Zhu et al. carefully stretched the 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[29]. 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 of the $k$ of the original fiber of 21 W/m·K. Structure investigation, including XRD, pole-figure of XRD, and polarized Raman, applied to this microfiber demonstrated that the crystallinity of the UHMW-PE microfibers decreases during stretching. The molecular chains in the amorphous region instead of the crystallites were better aligned along the stretching/axial direction and the local high thermal conductivity of the molecular chain devoted greatly to the enhancement of the overall thermal conductivity in this microfiber. It is the first time that a very high thermal conductivity of PE microfiber was achieved at reduced crystallinity and directly confirmed the amorphous alignment's contribution to $k$ increase. Latter such mechanism and structure was confirmed in Xu's work[59]. However, the elevated temperature selection and controlling in hot stretching has significant effects on the final product which varies from sample to sample.
Cold drawing process could also help align the orientation of the crystallites in the fiber. The polymeric fibers and strips are stretched at room temperature in cold drawing. The crystallites will orient along the deformation direction according to the stress and strain. Nitta et al. investigated the tensile behavior of cold-drawn isotactic polypropylenes (iPP)[60]. Their result showed that the fragmented lamellar clusters were first aligned tightly in the necking region and the further elongation in post necking region was caused by the amorphous region between the crystalline lamellae and strain hardening happened after that. Xiao et al.[61] cold-stretched PANI film at room temperature with different levels of strains. They found that the molecular chains and crystallites were forced to align along the stretching direction. Besides, 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 $k$ improvement

After structure tailoring, it is critical to investigate the crystallinity, crystallite orientation, and other structure characteristics. x-ray diffraction (XRD), pole-figure of XRD, and polarized Raman are preferable tools for this characterization. XRD is a well-known technique for structure characterization including crystal orientation, grain size, and crystal defects, etc.[62]. Its mechanism can be simply described as that the 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’s work, XRD pattern of the UHMW-PE fiber bundles (Fig. 5) shows the multiple diffraction peaks for the PE fiber bundle. Each diffraction peak position could be used to calculate 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 devote to the elongation of mean free path of phonons in the PE fiber.

![XRD pattern for the UHMW-PE fiber bundles.](image)

Figure 5. XRD pattern for the UHMW-PE fiber bundles. The pattern before and after stretching does not show obvious difference, illustrating the conservation of its original crystalline structure.

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In the 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 the fiber, XRD pole figure will fix the incident X-ray and the detector, and rotate the sample to investigate the variation of diffraction along the rotating angel. Zhu et al. has used pole figure patterns of (002) plane of UHMW-PE to clarify the fact that no obvious enhancement occurred in the crystal orientation. As shown in the 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 above XRD pattern study. Thus, Zhu et al. concluded
that the alignment of the amorphous region could significantly improves the overall thermal conductivity rather than the crystal region in such fibers of high crystallinity.

Figure 6. XRD pole figures for (002) plane of the stretched sample (a) and the reference one (b) shows no big difference. (c) Schematic of pole-figure XRD. (d) Intensity variation with varying $\beta$. [Reprinted with permission from Ref. [29]. Copyright (2017) American Chemical Society].
Besides XRD technology, polarized Raman spectroscopy can detect the molecular orientation in addition to providing the chemical bonds and structure information. In polarized Raman, the intensity of 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[63]. When the vibration direction is the same, the fluctuations in the polarizabilities of molecular vibrations could be detected and the corresponding Raman peak appears in the Raman spectrum. The variation in polarizabilities does not occur as the molecular vibration direction is perpendicular to the incident electromagnetic field. Zhu et al. used polarized Raman to measure the direction of the crystallites in the UHMW-PE fiber before and after stretching[29]. The result is shown in Fig. 7. The polarization direction was rotated and denoted by using the angle \( \gamma \) between the axis direction of the fiber and the laser polarization. As the laser polarization was rotated from 0\(^{\circ}\) to 90\(^{\circ}\), the crystalline band 1416 cm\(^{-1}\) became weaker but the amorphous bands at 1440 cm\(^{-1}\) and 1460 cm\(^{-1}\) increased obviously. The comparison between the normalized intensity of the polarized Raman results from the polymers before and after stretching in Figs. 7(b) and (c) illustrates the increment in the amorphous phase and their alignment.
Figure 7. (a) Polarized Raman spectra measured from an UHMW-PE microfiber before and after stretching. The difference in the normalized intensity between before (b) and after (c) stretching.
illustrate the structure change in the UHMW-PE microfiber. [Reprinted with permission from Ref. [29]. Copyright (2017) American Chemical Society].


4.1. Techniques for thermal characterization: a general picture

It has been well known the thermal properties measurement is critical for deeply understanding the thermal property of polymers under structure tailoring. The methods measuring the thermal conductivity/thermal diffusivity of polymers include the Time-Domain Thermo-Reflectance method (TDTR)[64], microfabricated-bridge method[65], pulsed photothermal radiometry method (PPTR)[36, 37], bi-material AFM cantilever method[58], and transient electro-thermal technique (TET)[66]. As shown in Fig. 8(a), the TDTR method depends on the principle that the change of reflecting probe beam intensity is proportional to temperature change of the metal transducer. The known quantities in the analysis are the heat capacity and thickness of each layer[67-69]. 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 could lead to 10% uncertainty in the thermal conductivity, which means that attention should be paid to the thickness of each layer to ensure accurate measurement. The advantage of TDTR is that it does not need the resistance-temperature calibration. It is like the photothermal technique[70-74] that operates in the frequency domain, but TDTR works in the time domain. TDTR has been proven to be a robust and routine method to measure the thermal conductivity of ultra-thin film and interface thermal conductance.
Figure 8. Schematic diagrams of experimental setups for the TDTR method (a) [Reprinted with permission from Ref. [75]. Copyright (2018) Materials Research Society] and the PPTR method (b) [Reprinted with permission from Ref. [76]. Copyright (1997) John Wiley & Sons, Inc.].

For the microfabricated-bridge method, the to-be-measured wire serves as the thermal bridge between two heater pads. These two heater pads also serve as 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[65]. It should be paid more attention to the thermal contact between the wire and the suspended devices when doing this experiment. The microfabricated bridge method can measure the thermal property of nanoscale wire while the fabrication of microdevice 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 detector[37]. By fitting the radiometry signal, the in-plane thermal diffusivity of measured sample can be determined[37]. The limitations of the PPTR occur when samples having low IR emissivity or low laser-damage thresholds. The experimental schematic of PPTR is shown in Fig. 8(b).
The bi-material AFM cantilever method for micro/nanofibers was developed in Chen’s group, and the detailed experimental setup could be found in ref. [58]. The sample bridged between a thermocouple and an AFM cantilever. The thermocouple was mounted onto the tip of a steel needle and could be heated by the needle to a desired temperature, while the cantilever was bi-material and its deflection was very sensitive to the power/energy variations. A laser beam was focused on the cantilever to record the deflection of the cantilever and the power variation due to temperature change 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 could be determined. The methods mentioned above all have their own advantages and disadvantages.

4.2. TET and PLRT2 techniques: high accuracy and ease of operation

Compared with TDTR and microfabricated bridge method, the TET technique developed by Wang’s group at Iowa State University is readily to build and no calibration required to measure the thermal diffusivity. Figure 9 shows the schematic of TET technique and the pulsed laser-assisted thermal relaxation (PLTR2) technique. In the TET experiment, the to-be-measured sample is suspended between two electrodes. The whole sample is placed in a vacuum chamber to eliminate the thermal convection. Since polymer is non-conductive, it should be coated with gold or other metal (~ nm thickness) first before the test. During the test, a DC current 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 \( T^* = (V-V_0)/(V_\infty-V_0) \),
with $V_0$ and $V_∞$ are the voltage of the sample before and after the 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

$$\frac{\partial \left( \rho c_p T \right)}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + q.$$  

(2)

Here, $\rho$, $c_p$ and $k$ are the density, specific heat and thermal conductivity of the sample, respectively. $q$ equals $P R / A L$, where $A$ and $L$ are the cross-sectional area and length of the sample, respectively.

The boundary condition and initial condition are $T(x=0, x=L) = T_0$ and $T(t=0) = T_0$, respectively.

The theoretical normalized temperature rise, which is defined as $T^*(t)=[T(t)-T_0]/[T(t→∞)-T_0]$, is solved as[66]

$$T^* = \frac{96}{\pi^4} \sum_{m=1}^{∞} \frac{1 - \exp[-(2m-1)^2 \pi^2 \alpha_{eff} t / L^2]}{(2m-1)^4},$$  

(3)

where $\alpha_{eff}$ is the sample’s effective thermal diffusivity that 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 $\alpha_{eff}$, and is compared with the experimental results. The trial value which gives the best fit of the experiment data is taken as the sample’s effective thermal diffusivity ($\alpha_{eff}$). The real thermal diffusivity of the sample can be obtained by subtracting the effect of radiation and gold coating, and the details can be found in the references[77-79].

The TET technique is mostly applied to analyze the in-plane thermal transport. Wang’s lab also developed the PLTR2 technique to investigate the cross-plane thermal transport[52]. The original
PLRT technique was also developed by Wang's lab that used a nanosecond pulsed laser to heat up a suspended sample and observe the temperature/voltage relaxation of the sample to determine its thermal diffusivity[80]. The experimental schematic of the PLTR2 is shown in Fig. 9. Before the test, the two sides of the P3HT film are coated with gold. Then the sample bridges between two electrodes. Silver paste is used to ensure low thermal resistance between the sample and electrodes. It is noteworthy that the topside gold film is in no contact with the electrodes. During the experiment, a nanosecond pulsed laser with 1064 nm wavelength irradiated the top side of the sample. The wavelength of the pulsed laser does not need to be 1064 nm as long as the gold film has high absorption at certain wavelength. At the same time, a constant DC current is fed through the gold film on the bottom to sense the temperature change. This DC current is carefully selected to ensure both perceptible voltage change and minimum joule heating. The voltage evolution of the bottom-side gold film is monitored by an oscilloscope.

In 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 in no contact with the electrodes, the thermal energy will transfer from the topside gold film to the P3HT film. This cross-plane thermal transport is proved to be extremely fast like hundreds of microseconds[52]. The cross-plane thermal diffusivity is derived as: $\alpha=1.38D^2/\pi^2t_{1/2}$[81], where $D$ is the thickness of the P3HT film and $t_{1/2}$ is the time taken to reach half of the maximum temperature rise. As shown in Fig. 9, the very fast cross-plane thermal transport part is followed by an in-plane thermal transport due to the heat dissipation from the P3HT film to the electrodes. As 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[52]:

$$
\alpha = \frac{1.38D^2}{\pi^2t_{1/2}}
$$
\[ \frac{\partial \left( \rho c_p T \right)}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + q_0, \quad q_0 = \begin{cases} q_{\text{laser}} + q_{\text{joule}}, & 0 \leq t \leq \Delta t \\ q_{\text{joule}}, & t > \Delta t \end{cases} \] (4)

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

\[ T^* = \frac{8}{\pi^2} \sum_{m=1}^{\infty} \exp \left[ -\frac{(2m-1)^2 \pi^2 \alpha t / L^2}{(2m-1)^2} \right] \] (5)

After obtaining the normalized temperature profile from experimental data, different values of the thermal diffusivity (in-plane) are tried to fit the normalized temperature. The value giving the best fit will be taken as the in-plane thermal diffusivity of the P3HT film.
Figure 9. Experimental schematic and physical principles of TET technique and PLTR2. [Reprinted from Ref.[52], Copyright (2013), with permission of Elsevier].
The TET technique and PLTR2 have been evaluated rigorously with sound accuracy and high reliability in Wang’s lab to characterize the thermal properties of various conductive and non-conductive micro/nanoscale fibers/films[52, 79, 82, 83].

Although thermal characterization seems straightforward, great cares have to be taken in experiment design and data analysis. In the past, the thermal conductivity of many polymers is incorrectly claimed due to the ignored or mistreated radiation effect, which will become dominant when the wire/film-like samples have a very high aspect ratio. Examples of the radiation effect rigorous consideration have been given in work by Wang's group[84]. Also heating rate evaluation and temperature measurement will become very challenging for techniques that rely on direct knowledge of the heating rate and temperature rise for direct thermal conductivity calculation. 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 proved to give some of the best accuracy measurement for fiber-like and film-like samples[66, 85] and are far superior to the 3ω technique[86].

4.3. Structure analysis based on phonon scattering: thermal reffusivity

It has been commonly recognized that thermal conductivity strongly depends on the micro/nanoscale structure of materials. However, if only having a look at the $k-T$ profile of the materials, very little information about the microstructure of materials can be obtained. Based on the mechanism of phonon scattering, 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.
to study the structure size in DNA[87]. Then it was developed and proved applicable in various materials like polymers, carbon-based materials[79, 83, 88, 89]. In this section, the focus is on the thermal reffusivity theory application in polymers’ structure improvement.

In non-metal materials, the 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 temperature decreases, due to the largely reduced phonon population, the phonon-phonon scattering becomes weak while the phonon-defect scattering becomes dominant.

For isotropic and non-metallic materials, the thermal reffusivity (Θ) was defined as: Θ=1/α. Here, α is thermal diffusivity. According to Mathiessen rule, considering different scattering mechanisms, the combined relaxation time (τ_c) can be written as:

$$\frac{1}{\tau_c} = \frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{imp}} + \frac{1}{\tau_{GB}} + \frac{1}{\tau_{surf}}$$

(6)

Here, ‘ph-ph’, ‘imp’, ‘GB’ and ‘surf’ indicate phonon-phonon scattering, phonon-impurity scattering, phonon-grain boundary scattering and phonon-surface scattering, respectively. Combining Eq. (6) with the definition of thermal reffusivity, Θ can be written as:

$$\Theta = 3\left(\frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{imp}} + \frac{1}{\tau_{GB}} + \frac{1}{\tau_{surf}}\right)^{-2}$$

(7)

Here, v is the phonon velocity. Eq. (7) can be rewritten as Θ= Θ_{ph-ph}+ Θ_0 if we regard all the impurities, grain boundaries, and surfaces as the defects. Θ_0 is the thermal reffusivity due to
phonon-defect scattering. $\Theta_{ph-ph}$ is the thermal reffusivity due to the phonon-phonon scattering. As temperature decreases to 0 K, the phonon-phonon scattering vanishes, the residual thermal reffusivity owes to the phonon-defect scattering. If there are rare chemical impurities and lattice defects in the materials, then the phonon-grain boundary scattering dominates at 0 K. Namely, $\Theta_0 = 3/(vl)$. Here, $l$ is the mean free path due to phonon-grain boundary scattering, which is proportional to the average grain size, or even very close to it. It is clearly seen that the residual thermal reffusivity is directly related with the grain size. The larger the grain size is, the smaller $\Theta_0$ is.

The thermal reffusivity theory can be applied to study the grain size of materials. As the $\Theta_0$ of carbon nanocoils was obtained from experiments, the grain size can be calculated according to Eq. (7). The thermal reffusivity of carbon nanocoils (a) and graphite (b) and graphene foam (c) are shown in Fig. 10. Deng et al. analyzed the grain sizes of carbon nanocoils by using the thermal reffusivity theory, Raman method and XRD, respectively. It is found that the grains size obtained by thermal reffusivity theory agrees well with those values obtained from Raman spectrum and XRD[90].
Figure 10. Thermal reffusivity of carbon nanocoils (a), Graphite (b) and Graphene foam (c) at different temperatures. [Reprinted with permission from Ref. [90]. Copyright (2016), American Chemical Society]

The thermal reffusivity theory can also be used to investigate the mechanism of thermal property improvement of the stretched polyethylene (PE) fibers. Zhu et al. studied the thermal properties and grain size of ultra-high molecular weight PE fibers under hot stretching[29]. Figure 11 shows the thermal reffusivity of the stretched and reference PE fibers. It is observed that the residual thermal reffusivity of the stretched PE fiber decreased compared with its reference. This indicates that the grain size increased after being stretched, which was verified by XRD[29]. Besides, the fitting curve of the stretched PE fiber changes more smoothly with temperature than that of reference. This is because that the Debye temperature decreases after being hot stretched[83].
Further structure analysis indicates that thermal diffusivity increase in the stretched samples is owing to the better alignment of the amorphous part in the PE fiber[29].

Figure 11. $\Theta$ changes with temperature for sample A, B and C: $\Theta_0$ is fitted from 4th-order polynomial regression. [Reprinted with permission from Ref. [29]. Copyright (2017) American Chemical Society]
In this work, the thermal reffusivity successfully evaluates structure improvement of the hot stretched PE fiber. The thermal reffusivity theory is applicable not only limited to polymers, it has been applied successfully in quantitatively analyzing the structural size and Debye temperature of carbon-based materials like graphene paper[83, 89] and carbon fiber[88]. In addition to semi-crystalline materials, the thermal reffusivity theory also successfully evaluates the structural domain size of human hair from Asian. It proves the thermal reffusivity is a powerful tool to analyze the structure of amorphous materials[89], though the important role of thermal reffusivity in analyzing the microstructure of various materials has been unaware by researchers in previous works. Due to the ultrathin scattering cross-section in 2D materials, such as graphene and MoS$_2$, the in-plane structure information is hard to directly obtain using traditional beam scattering methods, like XRD. Instead, the thermal reffusivity near 0 K provides a very promising tool 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 physic principles have been summarized in this review. Methods for fabricating and structure tailoring, including compression molding, injection molding, electrospinning, stretching and coating methods were reviewed based on these four principles. Additionally, some widely used thermal probing techniques, the transient electro-thermal (TET) and pulsed laser-assisted thermal relaxation 2 (PLTR2) techniques were also reviewed for multi-dimensional thermal probing at the micro/nanoscale. The TET and PLRT2
techniques provide some of the best accuracy measurement of thermal conductivity of polymers in the form of wire and films.

Though crystalline structure is preferred for achieving high thermal conductivity of polymers, the high crystallinity will reduce the flexibility of polymers, which makes the polymeric products brittle. Utilizing the alignment of molecular chain along the desired directions in amorphous regions will provide a great potential for enhancing the thermal conductivity without much sacrificing the mechanical properties. The detailed mechanisms of polymer chains conducting heat remain a challenge and need more efforts to explore and even control. Furthermore, there are numerous challenges to be resolved before industry can go on with the mass production of structure-tailored polymers with high thermal conductivity. Current structure tailoring of polymers has been limited to thin films or micro/nanofibers. This significantly limits the application. It is critical to tailor the structure of bulk polymers (3D) toward broader applications. To better control the thermal performance of fabricated polymers, novel thermal measurement techniques are still highly demanded which could flexibly fit in the in-situ measurement in different structures at small scales.

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