Highly Thermal Conductive Polymer Chains with Reactive Groups: A Step Towards True Application

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Abstract: Nanostructured polyethylene (PE, [-CH$_2$-CH$_2$]$_n$) films with metal-like thermal conductivity have opened the opportunities for polymers in advanced thermal management. However, in practice, polymers used in thermal management are either thermoset or at least stable at high temperature, for which 150~180 °C is typical. Thus PE as a thermoplastic polymer, whose softening temperature is ~120 °C, is not applicable in real use. Thus here we introduce a simple reactive group -OH to each segment of the PE chain [-CH$_2$-CH$_2$]$_n$ to form [-CH$_2$-CHOH]$_n$, which turns the polymer into polyvinyl alcohol (PVA) indeed, as a step towards the thermoset system. Our calculations show that for aligned PVA chains, the thermal conductivity can reach 8.49 W/m-K (infinite
chains), and experiments verify this by achieving a thermal conductivity of 8.51 W/m-K in a PVA film consisting of chain-aligned nanofibers. The alignment degrees of the PVA chains in the nanofibers are especially investigated to elucidate the nanostructure of the film, and the phonon dispersion and transport are also discussed. This work is intended to stimulate further trial into the development of high thermal conductivity polymer materials towards real uses and true application scenarios.

Introduction

Polymers of good flexibility and moldability are widely used in heat conductive materials as the matrix for the metal and ceramic powders.\textsuperscript{1-3} However, polymers with low thermal conductivity (\textasciitilde0.2 W/m-K) are also considered as the main conductive bottleneck in applications such as thermal interface materials (TIM),\textsuperscript{4, 5} moulding compound,\textsuperscript{6} printed circuit board (PCB)\textsuperscript{7, 8} and, etc.

Although bulk polymer materials are generally regarded as poor heat conductors, an individual polymer chain or a chain-aligned polymer fiber are believed to have very high thermal conductivity.\textsuperscript{9, 10} Researchers believe excellent thermal conductivity can be
realized by assembling the units in order.\textsuperscript{11} To date, most of the theoretical and practical interest focuses on polyethylene (PE) due to its model simplicity and its C-C bond similarity to diamonds, one of the most thermal conductive (above 1000 W/m-K) material in nature.\textsuperscript{12} The long carbon chain of PE serves as an efficient phonon transport path along the axis. Theoretically, The numerical predictions for the thermal conductivities of PE single polymer chain and for a PE single-crystal are >100 W/m-K\textsuperscript{7} and 273 W/m-K.\textsuperscript{13} Practically, the thermal conductivities of PE fibers and films can achieve respectively 104 W/m-K\textsuperscript{14} and 62 W/m-K.\textsuperscript{15}

However, this exceptionally high thermal conductivity will not qualify PE for real thermal management applications, because its softening point is \textasciitilde120 °C,\textsuperscript{16} lower than the aging condition of most application scenarios (150~180 °C). Therefore, the research interest should move to the search for thermostable polymers. There are two routes to achieve this in state-of-the-art applications. One is to use thermoset materials (with reactive group), e.g. epoxy or rubber. The other is to use non-reactive but thermostable polymers, e.g. dimethyl silicone oil (>200 °C stable). For carbon chain polymers, thermoset seems to be the only option. Thus our research started here.
The first candidate came into our vision is poly (vinyl alcohol) (PVA, [-CH$_2$-CHOH-]$_n$), because its melting point is above 200 °C$^{17,18}$ and it introduces only a minor change to the carbon chain of PE ([-CH$_2$-CH$_2$-]$_n$) by replacing a hydrogen (–H) with a hydroxyl (–OH)$^{19}$ in each segment. Literatures$^{20,21}$ show that this replacement should result in the evolution of phonon dispersion curve (Figure 1a). In the low-frequency range, the group velocity of PVA drops dramatically compared to PE, which could be mainly attributed to the strong phonon-scattering effect by the heavy –OH branches.$^{20}$ Thus we can expect a drop in thermal conductivity by introducing –OH. But how large the drop is and how this would threaten the prospect of the highly thermal conductive polymer in the true application is yet to be clarified.

Here, we report a consistent result of the PVA thermal conductivity from both theoretical and experimental studies. For aligned PVA chains (infinite length), the theoretically thermal conductivity is calculated as 8.49 W/m-K, while the thermal conductivity of the as-fabricated nanostructured film is measured as 8.51 W/m-K, over one order of magnitude larger than the reported ~0.3 W/m-K of amorphous PVA material.$^{22}$ Since the chain alignment is crucial to explain the structural property
relationship, we have also investigated the phonon densities of states (PDOS) of aligned polymer chains in theory and developed polarized Fourier transform infrared (FTIR) method to measure the chain alignment in the experiment. This method is a good complement to the wide-angle X-ray scattering (WAXS) method at low chain orderness or crystallinity. We understand that the –OH groups (at a near-right angle to C-C main chain) in PVA break the symmetry of PE chains. This enables the polarized FTIR method to discern alignment degree differences at even low orderness, for which, the WAXS signal is not distinct. Moreover, for nanofiber alignment characterization, we have developed a laser diffraction (LD) method to monitor the film quality on-line. This work shows promising progress in high thermal conductivity polymers with reactive groups, which is a step forward to the true application, particularly when thermal stability is required.

Results and discussion

Simulation of PVA thermal conductivity. Here we used the Non-equilibrium molecular dynamics method (NEMD)\textsuperscript{23, 24} to calculate the thermal conductivity ($\kappa$) of amorphous
PVA and chain-aligned PVA. For amorphous PVA, the thermal conductivity is 0.253 W/m-K, while for chain-aligned PVA, the thermal conductivity increases as the chain length ($L$) increasing (Figure 1b) and finally converges to 8.49 W/m-K at infinity. To shed some light on this contrast, phonon DOS (PDOS) of C atoms and O atoms in amorphous PVA and chain-aligned PVA were calculated by Green’s function-based molecular dynamics (GFMD$^{25}$) method and the results are demonstrated in Figure 1c&d. The PDOS of C atoms in the aligned PVA chains is much greater than that in the amorphous PVA chains at a lower frequency, while PDOS of O atoms shows a similar phenomenon but much less significant. Since low-frequency phonons transport further and thus are more important contributors to thermal conductivity, this PDOS evolution accounts well for the enhancement of thermal conductivity by chain aligning.
Fig. 1 (a) Phonon dispersion curves of PVA\textsuperscript{20} and PE\textsuperscript{21} in the orthorhombic lattice. (b) Effect of chain length \((L)\) on thermal conductivity \((k)\). (c) PDOS of carbon atoms in chain-aligned and amorphous PVA. (d) PDOS of oxygen atoms in chain-aligned and amorphous PVA.

**Fabrication of PVA nanofibrous films.** Motivated by the theoretical results, we fabricated nanostructured polymer films using a 3-step method (Fig. 2): (1) Disentangling chains: ultrasonic pretreatment was used to disentangle the chains in the spinning solution and
thus help align the chains during electrospinning; (2) Aligning fibers: modified electrode collectors were used to align continuous nanofibers during film-forming process; (3) Stretching film: hot-stretching was applied to the nanostructured polymer films for further increase of the chain and fiber alignment.

**Fig.2** Schematic of the 3-step method for PVA nanostructured film fabrication.

**Characterization of chain alignment.** When the sample orderness is low, ordinary crystallinity measurement like WAXS cannot discern the chain alignment details (Fig.S5, Supporting Information), which is a technical gap we need to fill. Considering that the –OH groups (at a near-right angle to carbon chain) in PVA break the symmetry that PE
preserves, which might bring about interesting changes in the FTIR spectra especially when the incident light is polarized, thus we used the polarized FTIR to study the structural differences between entangled and disentangled chains. We luckily found some distinct changes in the spectra. We believe this method can be extended to carbon chain polymers with other unsymmetrical branches and thus is a powerful tool for chain alignment study when the sample orderliness is far from crystalline.
Fig.3 (a) FTIR spectra of entangled and disentangled PVA chains (b) Configuration of polarized IR—parallel ($\parallel$) and perpendicular ($\perp$). (c) Polarized FTIR spectra of entangled PVA chains. (d) Polarized FTIR spectra of disentangled PVA chains. All samples were prepared in the form of film.

Fig.3 presents the structural information of PVA nanostructured film with entangled and disentangled chains fabricated by electrospinning. The –OH branches introduce lots of hydrogen bonds into the system, which cause severe chain entanglement and restrain chains from aligning during the electrospinning process. In step 1, we used high power ultrasonic pretreatment to break the hydrogen bonds and disentangle the polymer chains in the spinning solution. Fig.3a shows the FTIR spectra of PVA nanostructured film with and without the disentangling process. We set the C–H stretching band (2912 cm$^{-1}$) as the benchmark, whose intensity barely changes during the disentanglement process. The large band observed between 3000 and 3600 cm$^{-1}$ is linked to the O–H stretching of hydrogen bonds. The intensity of this band decreases greatly after the ultrasonic pretreatment, indicating the decrease of hydrogen bonds. This may result in a
better chain alignment in the following electrospinning process, which could be further confirmed by the polarized FTIR. Fig.3b demonstrates the configuration of polarized FTIR and Fig.3c&d give the results. In Fig.3d, the C-C stretching band (1143 cm\(^{-1}\)) of disentangled sample presents a distinct anisotropic feature: the perpendicular (\(\perp\)) polarized band intensity is much lower than the parallel polarized (\(//\)) one (Fig.3d), which is not observed in the entangled film (Fig.3c). Therefore, the disentangling pretreatment on polymer spinning solution should significantly enhance the chain-aligning efficacy of electrospinning.
Fig. 4 (a) Illustration of LD system and WAXS method setups. (b) SEM images (inlet I~III), LD patterns (inlet IV~VI), WAXS patterns (inlet VII~IX) and thermal conductivities of nanostructured films of different alignment degrees ($f$).

**On-line monitoring of fiber alignment.** Besides the chain alignment, the fiber alignment is also crucial to the thermal conductivity of the nanofibrous film. Thus during the electrospinning process, a pair of parallel electrode collectors were used to align the fibrous film layer by layer, and a laser diffraction (LD) system (Fig. 4a) was set up for on-line monitoring of the fiber alignment. The diffraction patterns mathematically are equal to the Fourier transform of the fibers arrangement patterns. In diffraction patterns, the orientation information is mainly reflected by the azimuthal intensity distribution. The alignment degree $f$, which is also called Herman’s Orientation Factor (HOF), can be calculated accordingly$^{30,31}$ (Supplementary Note 3, Supporting Information). The $f$ value ranges from 0 to 1, representing random to perfect alignment. For films of different $f$ (Fig. 4b inlet I~III), the LD diffraction patterns (Fig. 4b inlet IV-VI) agree well with the WAXS patterns (Fig. 4b inlet VII~IX) and the Fourier transform patterns of the SEM images.
(Fig.S6, Supporting Information), yet this method is low-cost, time-saving and on-line. The real-time feedback of alignment information provided by this system helps the on-line adjustment of experimental parameters.

Fig.5 (a) WAXS patterns of nanostructured films at different draw ratios. (b) Thermal conductivity and orientation distribution functions (ODF) as a function of draw ratio ($\lambda$).

**Thermal conductivity measurement.** Fig.4b also exhibits the structural property relationship of different $f$ values. The highly aligned PVA nanostructured film with $f=0.88$ has the highest thermal conductivity (3.42 W/m-K), about eight times higher than that of randomly aligned nanostructured film (0.41 W/m-K, $f=0.09$). This is much less than
expected ~8.49 W/m-K. The reason is given by the WAXS pattern (Fig.4b inlet IX), that although the fibers alignment is well controlled, the chains alignment is not as good. To achieve a higher chain alignment degree, hot stretching is thus conducted. The nanostructured film with  \( f=0.88 \) was stretched at 200 °C in air. SEM images (Fig.S4, Supporting Information) present that after hot stretching, the fibers became slimmer while their alignment was enhanced. The measured thermal conductivity as a function of draw ratio \( (\lambda) \) is depicted in Fig.5. The thermal conductivity increases as the draw ratios increase, from 3.71 W/m-K \( (\lambda=1) \) to 8.51 W/m-K \( (\lambda=12) \). The corresponding WAXS patterns are also presented in the left column in Fig.5. The pattern transition from discontinuous rings \( (\lambda=1) \) to discrete long arcs \( (\lambda=4) \) to short arcs \( (\lambda=12) \) indicates the chain alignment is improving continuously. And the orientation distribution functions (ODF, value from 0~1)\(^{32} \) calculated from WAXS patterns (method see Supplementary Note 3, Supporting Information) are also depicted in Fig.5. The ODF changes greatly from 0.40 to 0.93, verifying a great enhancement of crystal quality. It is noteworthy that here the ODF accounts for two origins of orientation. One is the chain orientation within each fiber; the other is the fiber orientation itself. Since the fibrous film we chose had a known fiber...
orientation as high as 0.88, and was merely enhanced to ~0.92 after the hot stretching (calculated from the Fourier Transformation of SEM image in Fig. S4, Supporting Information), thus the large change in ODF mainly comes from the chain orientation improvement. We also notice that the increasing trend of thermal conductivity seems unsynchronized with the orientation increase. When the ODF increases from 0.4 to 0.84, the thermal conductivity increases mildly from 3.42 W/m-K to 5.69 W/m-K. On contrast, the last increase of ODF from 0.84 to 0.93 leads to a leap of thermal conductivity from 5.69 W/m-K to 8.51 W/m-K, implying that the phonon excitation and transport are significantly boosted due to final effort of orientation.

**Discussion and prospect.** The thermal conductivity of polymers can be obtained from the Debye equation,  

\[
k = \frac{1}{3} \sum_j \int C_j(\omega) v_j \ell_j(\omega) d\omega
\]  

(1)

where \(C_j(\omega)\) as a function of phonon frequency \(\omega\), is the specific heat capacity of phonons, which is positively related to PDOS; \(v_j\) is the phonon group velocity, which is strongly related to the strength of backbone bonding; \(\ell_j(\omega)\) is the phonon mean free path,
generally decreasing with $\omega$ and very sensitive to any phonon-scattering effect. Compared with PE, the PDOS of PVA drops in the low frequency range (Figure S2, Supporting Information). Figure 1a shows a decrease in $\nu_j$ of PVA. Moreover, the $\ell_j$ in PVA should be significantly shortened since the large amount of side amount of side –OH branches and the resulting hydrogen bonds are both strong phonon-scattering sources. Based on the above three reasons, a decrease in thermal conductivity is destined after the introduction of –OH. But according to our work, the thermal conductivity for aligned PVA chains remains a relatively high value as ~8.49 W/m-K, which is comparable with most thermal interface composites. Also the as-fabricated PVA film can withstand 180 °C high temperature, which promises its future in thermal management applications.

Moreover in real applications, fillers are usually incorporated into the polymer matrix to reduce the coefficient of thermal expansion (CTE) and enhance the thermal conductivity. In this situation, the presence of reactive group -OH may not only help enhance the thermostability but also help couple the polymer and the inorganic filler surface to reduce the interfacial thermal resistance. For chain-aligned PVA-based
composite materials, the filler influence on the thermal conductivity, thermal expansion, interfacial problems, chain orientation awaits more systematic investigation.

Conclusions

In summary, we have completed a pioneering joint work of theory and experiment on highly thermal conductive polymer chains with reactive groups, which is a step forward towards true application in thermal management. PVA ([-CH₂-COH-]ₙ) nanostructured film with thermal conductivity of 8.51 W/m-K was achieved by a 3-step method. Phonon density and transport behavior of PVA were studied in detail. A combination of polarized FTIR, WAXS and real-time LD was developed to determine the alignment degree of chains and fibers, which may provide a full solution on alignment characterization for other polymer systems. This work is intended to stimulate further trial into the development of highly thermal conductive polymer materials towards true thermal management application scenarios, such as PCB and TIM.

Experimental section
Calculation of thermal conductivity and PDOS. NEMD\textsuperscript{23} was used to predict the thermal conductivity of PVA. NEMD requires the use of a temperature gradient, which was realized by fixing different temperatures at two ends of the calculated system. The heat flux driven by the temperature gradient was then acquired. The thermal conductivity was calculated accordingly based on Fourier's law.\textsuperscript{36, 37} GFMD simulation\textsuperscript{25} was used to calculate the PDOS of crystalline and amorphous PVA based on the fluctuation-dissipation theory in this article. Green’s functions in reciprocal space can be obtained from the Fourier transform of the lattice displacements using molecular dynamics (MD).\textsuperscript{38} Then force constant matrix and dynamical matrix were obtained. The eigenvalues of the dynamical matrix were used to compute the PDOS. See Supplementary Note 1 (Supporting Information) for more details.

Fabrication of thermally conductive PVA nanostructured films. The films were fabricated by a 3-step method. The steps are (1) Disentangling chains: high-power ultrasonic pre-treatment was applied to the 10 wt.% PVA (Mw \textasciidetilde145,000, L\textasciidetilde1000 nm) solution; (2) Aligning fibers: aligned continuous nanofibers were produced by the electrospinning (ET-2535H, Ucalery) and collected by two parallel electrodes; (3)
Stretching film: the nanostructured polymer films were mechanically stretched at ~200 °C (infrared heating chamber, 300 W) and the stretching rate is about 1 cm/min. See Supplementary Note 2 (Supporting Information) for more details.

Alignment measurement. Polarized FTIR spectroscopy (Nicolet IS50) was used to study the optical anisotropy of the polymer sample at the molecular level to evaluate the chain alignment. WAXS (Rigaku with a 2-D detector Pilatus 200K) measurements were used to determine the crystallite orientation and crystallinity of films. Laser diffraction (LD) system was set up for on-line monitoring of the fiber alignment degree. See Supplementary Note 3 (Supporting Information) for more details including light parameters used and orientation factors calculation.

Thermal conductivity measurements. The thermal conductivities \(k = \rho C_P \alpha\)\(^{39}\) of PVA fibers were obtained by separately measuring the diffusivity \(\alpha\), density \(\rho\), and heat capacity \(C_P\). Here \(\alpha\) was measured by Angstrom method, which could also be measured by 3\(\omega\)-\(T\) method,\(^{40}\) \(\rho\) was measured by using the draining method (ME204, Mettler Toledo), and \(C_P\) was measured by Differential Scanning Calorimeter (DSC3, Mettler Toledo). The measurement platform for the Angstrom method is homemade. See
Supplementary Note 4 (Supporting Information) for more details on its setup and calibration.

Conflicts of interest

There are no conflicts to declare.

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