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Pore-Confined Polymers Enhance the Thermal Conductivity of Polymer Nanocomposites

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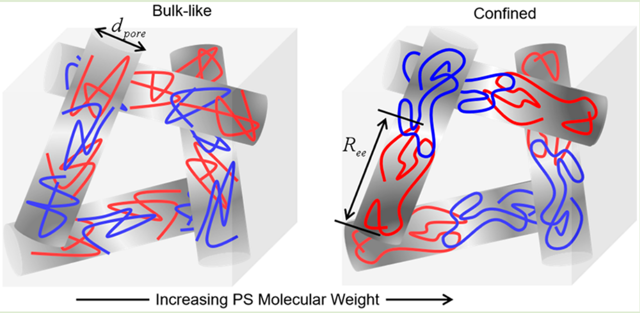
ABSTRACT: Molecularly confined polymer fillers in nanopores were found to give superior mechanical properties of polymer nanocomposites. In this work, we study the thermal conductivity of such nanocomposites and unveil the effect of polymer confinement on thermal conductivity. Using the time-domain thermoreflectance method, we measure the cross-plane thermal conductivity of polymer nanocomposites that consist of polystyrene fillers confined within a nanoporous organosilicate matrix. Compared to unconfined bulk polystyrene fillers, we find that pore-confined polystyrene fillers enhance the thermal conductivity of the polymer nanocomposites. This enhancement is attributed to the better aligned and less entangled chains in the confined phase, where chain−chain phonon scatterings are reduced. Our work provides essential insights into the thermal conductivity of polymer nanocomposites for multifunctional thermal and mechanical applications.



Polymers, as an exciting class of soft matter, have attracted increasing attention due to their unique properties. In particular, the knowledge of their thermal conductivity (k) is the key to many applications such as thermal diodes,[1] biosensors,[2] and electronic devices.[3] The k of polymers strongly depends on their topology and morphology.[4−7] For example, bulk polymers typically have low k on the order of 0.1 W/(mK) and are considered as thermal insulators mainly due to the inefficient chain−chain heat conduction via weak van der Waals interactions.[8] In contrast, the k of ultradrawn polyethylene can be as high as 42 W/(mK) in the orientational direction.[9] Moreover, well-aligned polyethylene nanofibers were reported to have a k of 104 W/(mK) along the drawing direction.[10] Ultrahigh in-plane thermal conductivity was found in 2D polymers,[6] and the all-directional thermal conductivity of the polymer was predicted in 3D covalent organic frameworks.[11] These results show that a thorough understanding of the structure−property relationship is crucial to achieving the desired k for a given application.

Polymer chain confinement plays a vital role in the morphology of polymers. Kraus et al.[12] studied confinement effects on the chain conformation in thin polymer films via diffuse neutron scattering and found that the in-plane dimension of the chains started to increase with decreasing film thickness below approximately $6R_g$ (where R_g is the radius of gyration). Using Monte Carlo simulations, Müller[13] found that chains did not overlap strongly and stretch parallel to the surface as the film thickness was reduced below R_g. Si et al.[14] reported that confinement could reduce interchain entanglements in the thin freestanding polymer films. Additionally, exceptional mechanical and fracture properties were reported for nanocomposites with molecularly confined polymers.[15,16] For the effect of polymer chain confinement on thermal transport, Liu et al.[17] experimentally observed that the thermal interface conductance between PS films and the substrate increased with decreasing film thickness when the thickness of the PS film was comparable to or smaller than the radius of gyration of bulk PS. We performed equilibrium molecular dynamics simulations to study the polymer chain confinement effect on k of amorphous ultrathin films and observed that stronger polymer confinement reduced k due to less efficient chain−chain heat conduction pathways.[5] However, the understanding of polymer confinement effects on k is still in its infancy, and their impact on k in other confined scenarios remains unknown.

In this work, we study the k of polymer nanocomposites using the time-domain thermoreflectance (TDTR) technique[18] to elucidate the confinement effects on k. By varying the molecular weight (M_w) of polystyrene (PS) filled in a nanoporous organosilicate matrix with fixed pore size, we

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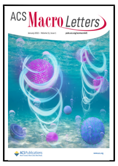

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find that confinement enhances k. Confinement in these pore-confined polymers results in better aligned chains, reducing intrachain and interchain phonon scatterings and increasing k. The knowledge from this study can help guide the design of pore-confined polymers for various applications. Combined with their mechanical strength, molecularly confined polymers may open up opportunities for thermomechanical applications.

The high-quality polymer nanocomposites composed of PS within a nanoporous organosilicate matrix with a mean pore diameter (d_{pore}) of 7 nm are fabricated. PS chains with different M_w are selected to fill a 50% porous ethylene oxycarbosilane (Et-OCS) matrix and obtain different degrees of confinement at the molecular level. The pores are randomly oriented in the 50% porous Et-OCS matrix, and the filling levels are 100% except for one molecular weight (M_w). The film thickness, filling level, density, and heat capacities of all the samples are summarized in Table 1. We include the unfilled nanoporous Et-OCS (sample 1) as a reference. Their density and thickness are measured by X-ray reflectivity (XRR). The surface roughness of all samples is smaller than 4 nm based on XRR data. The overall heat capacities of nanocomposites are estimated by averaging the heat capacities of both components. All the detailed information on the sample synthesis and characterization could be found in the Supporting Information (SI). To achieve high-quality samples, the optimal filling time and temperature are used for each M_w. The film thicknesses of all the samples are over 500 nm, which are large enough to rule out the size effects on thermal conductivity. The k's of all of the samples are measured by the TDTR method, which is becoming one of the standard techniques for characterizing thermal properties of bulk and thin films using ultrafast lasers.[18−21] We prepared 1 or 2 samples with centimeter size for each type and performed TDTR measurements on multiple spots for each sample. Details of these measurements are described in the SI.

Table 1. Film Thickness, Filling level, Density, and Heat Capacity of the Unfilled Nanoporous Et-OCS (Sample 1) and Four Sets of PS-Filled Nanocomposites (Samples 2−5)

sample	PS filler morphology	PS filler M_w (kDa)	filling level	thickness (nm)	density (g/cm^3)	heat capacity (J/(cm^3))
1	N/A	N/A	N/A	582	0.821	0.91
2	bulk-like	2	100%	555	1.313	1.51
3	transitional	10	100%	570	1.326	1.52
4	confined	90	88%	574	1.255	1.44
5	confined	400	100%	553	1.320	1.52

Figure 1a shows a TEM image of a 50% randomly porous and unfilled Et-OCS matrix with a mean pore diameter (d_{pore}) of 7 nm. The root-mean-square (RMS) end-to-end distance (R_{ee}) of polymer chains is a measure of molecular size, and it is defined by $R_{ee} = a\sqrt{N}$, where a is the Kuhn length[22] and N is the number of Kuhn monomers. When $R_{ee} \ll d_{\text{pore}}$, the polymer chains are bulk-like; when $R_{ee} > d_{\text{pore}}$, the polymer chains are confined. R_{ee} increases as the M_w of PS increases. The detailed relationship between R_{ee} and M_w of PS can be directly found in Figure 2 of ref 15. Within a fixed pore size of d_{pore} = 7 nm in this study, PS chains with $M_w \ll$ 11 kDa are bulk-like, while PS chains with $M_w >$ 11 kDa are subject to confinement, as illustrated in Figure 1b and 1c.

The measured k's of all four polymer nanocomposites are shown in Figure 2. The total uncertainties are obtained by adding the systematic uncertainties and experimental uncertainties, which are shown as error bars in the figure. The k of the unfilled nanoporous Et-OCS is 0.19 ± 0.02 W/(mK), which is lower than reported values of ~0.3 W/mK for similar

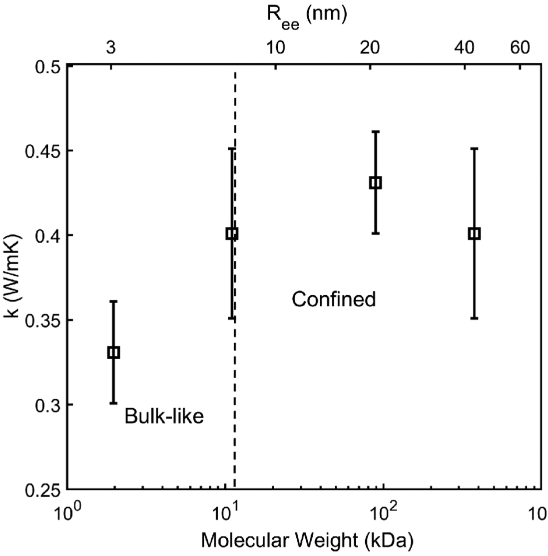

Figure 2. Measured thermal conductivity (k) of nanocomposites as a function of molecular weight (M_w) (bottom x axis) and RMS end-to-end distance (R_{ee}) (top x axis) of PS fillers. Note that the average pore size of the Et-OCS matrix is 7 nm, and the vertical dashed line is used to distinguish bulk-like and confined regimes.

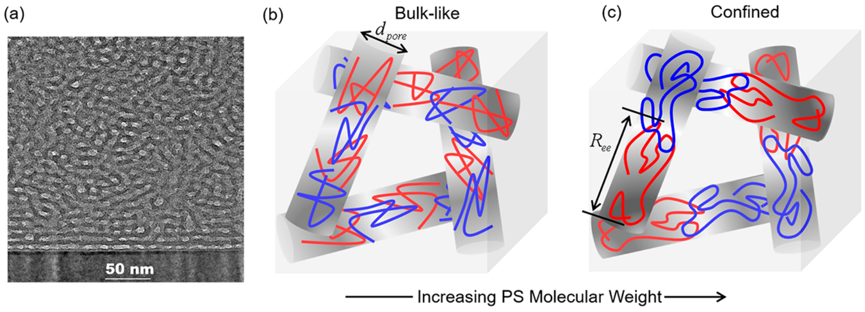

Figure 1. (a) TEM image of a 50% randomly porous and unfilled ethylene oxycarbosilane (Et-OCS) matrix with a mean pore diameter (d_{pore}) of 7 nm. (b) and (c) Illustration of the state of PS with different molecular weight (M_w) filled in the Et-OCS matrix.

oxycarbosilane materials due to the large porous volume in our sample.[23,24] The k of PS-filled Et-OCS nanocomposites is larger than that of the unfilled Et-OCS matrix because of increased density and heat capacity. Moreover, nanocomposites with confined PS fillers show larger k than nanocomposites with bulk-like PS fillers. To better highlight the relationship between k and the confinement level, we also plot k with respect to R_{ee} as the top x axis in Figure 2.

To understand why nanocomposites with confined PS fillers give higher k, we further calculate the k of PS fillers in nanocomposites using effective medium theory (EMT) and plot them as red circles in Figure 3. EMT has been demonstrated as an effective method to calculate the thermal conductivity of a heterogeneous material in which the two components are distributed randomly.[25−27] The details of the EMT are given in the SI. The bulk-like PS filler (M_w = 2 kDa) shows a k of 0.16 ± 0.04 W/(mK), in good agreement with k = 0.14 ± 0.01W/(mK) of bulk PS measured by Xie et al.,[28] k = 0.15 W/(mK) of bulk-like PS films measured by Jun et al.,[17] experimental k = 0.16 W/(mK) of bulk PS,[29] and k = 0.15 ± 0.02 W/(mK) of bulk PS calculated by Feng et al.[30] Confined PS fillers have a k of ~0.28 W/(mK) (red box in Figure 3), which is 75% larger than bulk-like PS fillers. PS with M_w = 90 kDa has the smallest density due to a lower filling level but the highest k likely because the smaller density makes the chains more stretched inside the pores. Because the confinement is achieved by increasing M_w, we need to make sure the enhancement of k does not come from increasing M_w itself. Therefore, we further include the reported experimental and calculated k of bulk PS with different M_w[17,28,30] as a comparison in Figure 3 (blue markers). It is shown that k of bulk PS is independent of M_w. Clearly, at the same M_w, the confined phase gives a higher k than its bulk counterpart. The gap between confined PS fillers and bulk PS marked by red and blue boxes in Figure 3 represents the k enhancement resulting from confinement effects of PS chains. With the same matrix, the enhanced k of confined PS fillers leads to a larger overall k of nanocomposites.

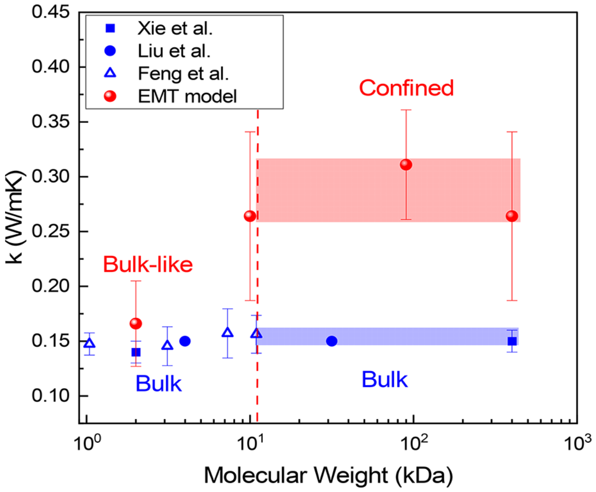

Figure 3. Thermal conductivity (k) of PS as a function of their molecular weight (M_w). Blue filled squares, blue filled circles, blue open triangles, and red spheres denote PS fillers in nanocomposites extracted from bulk PS measured by Xie et al.,[28] bulk-like PS films measured by Liu et al.,[17] and bulk PS calculated by Feng et al.,[30] respectively. The red dashed line distinguishes the bulk-like regime and the confined regime in PS fillers. The gap between red and blue boxes denotes the thermal conductivity enhancement resulting from the confinement effect.

Why does confinement in PS lead to a larger k? Although those pores are randomly oriented as shown in Figure 1a, the nanocomposites' overall k increases as long as k of each building block (each pore) increases. In the bulk phase, the PS chains are entangled inside each pore. As the M_w increases and reaches the confinement regime ($R_{ee} > d_{pore}$), the conformational changes happen to reduce the pervaded volume of the chain and exclude other chains to enter the pore, resulting in less interchain entanglements.[15,31,32] The chains find themselves in a more aligned configuration within the pores, as shown schematically in Figure 1c. This alignment leads to less intrachain and interchain phonon scattering[33] and thus larger k along the pore axis. The collective improvement in heat conduction path in each pore leads to the overall increase in k. This conclusion is along the same line as the increased k reported for ultradrawn polymer fibers because of chain alignment.[10] This is different from our previous work on ultrathin amorphous polymer thin films[5] because the confinement was achieved under different conditions. In our previous work, by reducing the film thickness without lateral constraints, one-dimensional confinement was created, and the polymer chains maintained amorphous states where the disentanglement of different chains reduces heat transfer from one chain to another. In this work, spherical pores connected by cylindrical necks force confinement of the polymer chains, and the alignment along the pore axis reassembles the ultradrawn polymer fibers.

In this study, TDTR is used to investigate the k of polymer nanocomposites with molecularly confined polymer fillers. By varying the M_w of PS chains introduced in a porous Et-OCS matrix, we study how chain confinement affects k. We find that k of the pore-confined polymers increases from its bulk counterparts. Because PS with large M_w has long polymer chains that are confined by the nanometer pores, these better-aligned polymer chains have reduced intrachain and interchain phonon scattering and thus increased k along the pore axis. Our experimental results demonstrate that molecular confinement can enhance thermal transport and provide useful insights into tailoring k of polymers for multifunctional thermal and mechanical applications. If we replace PS with polymers of higher conductivity in the crystalline phase, such as polyethylene, we expect the molecular confinement can lead to even larger thermal conductivity enhancement for the nanocomposites.

■ ASSOCIATED CONTENT

SI Supporting Information

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Sample synthesis and characterization, TDTR measurement, and effective medium theory (PDF)

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Author Contributions

H.M. and Z.T. conceived this study. K.L. and T.M. prepared samples. J.G., P.H., and S.H. helped with TDTR measurement. All authors read and approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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