Contact Thermal Resistance between Silver Nanowires with Poly(vinylpyrrolidone) Interlayers

Matthew L. Fitzgerald, Yang Zhao, Zhiliang Pan, Lin Yang, Shihong Lin, Godfrey Sauti, and Deyu Li*

ABSTRACT: Various nanofillers have been adopted to enhance the thermal conductivity of polymer nanocomposites. While it is widely believed that the contact thermal resistance between adjacent nanofillers can play an important role in limiting thermal conductivity enhancement of composite materials, lack of direct experimental data poses a significant challenge to perceiving the effects of these contacts. This study reports on direct measurements of thermal transport through contacts between silver nanowires (AgNWs) with a poly(vinylpyrrolidone) (PVP) interlayer. The results indicate that a PVP layer as thin as 4 nm can increase the total thermal resistance of the contact by up to an order of magnitude, when compared to bare AgNWs, even with a larger contact area. On the other hand, the thermal boundary resistance for PVP/silver interfaces could be significantly lower than that between polymer—carbon nanotubes (CNTs). Analyses based on these understandings further show why AgNWs could be more effective nanofillers than CNTs.

POLYMER COMPOSITES

Polymer composites are widely used materials because of their abundance, desirable mechanical properties, and relatively low cost; however, the normally low thermal conductivity of polymers (∼0.1 W/(m·K)) limits their applications in electronic devices and heat exchangers where efficient heat transfer is essential. Not surprisingly, extensive efforts have been put forth in seeking thermally conductive polymer composites, and over a half-century of research has been devoted to improving composite thermal conductivity by introducing thermally conductive fillers into host polymeric matrices. These polymer composites have been implemented in a variety of systems such as sensors, flexible electronics, and thermal interface materials, where heat dissipation is critical to device performance. However, so far, the overall thermal conductivity improvement of many polymer composites remains quite limited.

One notable example is CNT–polymer composites. Despite the exceptionally high thermal conductivity of CNTs (>3000 W/(m·K) for high-quality, thin tubes), many studies with CNTs embedded in a polymer matrix only show marginal thermal conductivity enhancement (<1 W/(m·K)), significantly lower than that predicted based on particle mixing theory. CNTs and other fillers randomly dispersed in a polymer matrix, the primary hurdle for enhancing the thermal conductivity has been thought to be the contact thermal resistance that exists between adjacent fillers and between the filler and polymer. In fact, it has been experimentally demonstrated that the contact thermal resistance between individual multiwall CNTs (MWCNTs) is much larger than the normally expected value as a result of the ~200 nm long phonon mean free path along the interlayer direction of MWCNTs (or c-axis of graphite) and phonon reflection from the innermost tube layer.

On the other hand, recent experimental results indicate that the contact thermal resistance between individual silver nanowires (AgNWs) could be ~20 times lower than that between similar diameter MWCNTs. In terms of thermal conductance per unit area, the value for contacts between AgNWs could be one order of magnitude higher than that between MWCNTs, which is partially due to lack of electron reflection back into the emitting wires. This is consistent with the higher thermal conductivity values typically displayed by polymer composites utilizing metallic nanofillers. However, one outstanding issue is that, in nanocomposites, the contact morphology between nanofillers could be much more complex, and instead of direct contacts between nanofillers, there is often a thin polymer layer between neighboring nanofillers. This thin polymer interlayer could enlarge the effective contact area between nanofillers but also poses additional thermal resistance. As such, it is important to explore how polymer interlayers alter the contact thermal resistance between nanofillers to better understand thermal transport in nanocomposites. This work presents measurements of contact thermal resistance between individual AgNWs with a thin PVP interlayer.

Received: March 14, 2021
Revised: April 19, 2021
Published: May 6, 2021
All thermal measurements were conducted using the well-established microthermal bridge method in a cryostat (Janis, Model CCS-400/204) under high vacuum (<1 × 10⁻⁶ mbar), which has been used to investigate thermal transport through various nanowires, including MWCNTs and AgNWs. A Wheatstone bridge circuit was adopted to cancel the baseline cryostat temperature fluctuation, leading to a thermal conductance measurement resolution of ∼85 pW/K at room temperature with the selected instrument settings. The background thermal conductance between the suspended membranes was measured and subtracted from the total thermal conductance to further increase measurement accuracy (see the Supporting Information). For the contact measurements, PVP was chosen as the polymer interlayer, because of its affinity with silver. To explore the contact thermal resistance between AgNWs with a PVP interlayer, electrospun PVP nanofibers were first measured to determine their thermal conductivity.

To prepare PVP nanofibers, PVP powder (Sigma–Aldrich, Lot No. 437190-25G, molecular weight: 1300 kg/mol) was dissolved in ethanol (Sigma–Aldrich, Lot No. 187380-1L) at a ratio of 1:10 (w/w), and the resulting solution was drawn into a 10 mL syringe through a 20-gauge needle. Electrosprinning was conducted at an operating voltage of 20 kV with a 50 μL/min flow rate, and the distance between the syringe tip and the grounded collector was 15 cm (see the Supporting Information for more details).

Figure 1a displays a scanning electron microscopy (SEM) image of an electrospun PVP nanofiber on the measurement device, while Figure 1b shows the measured thermal conductivity of PVP nanofibers with different diameters and suspended lengths. The average thermal conductivity at 300 K was measured to be 0.23 ± 0.02 W/(m·K), and no obvious trend exists for the various suspended lengths and diameters, indicating negligible contact thermal resistance between the suspended PVP fibers and the heat source/sink.

The measured nanofiber thermal conductivity is slightly lower than that of PVP thin films prepared by spin-coating of PVP solution (molecular weight: 25 kg/mol), as reported by Xie et al. This indicates that the thermal conductivity of the PVP nanofibers experiences little enhancement as a result of electrosprinning, in contrast to the case of polyethylene. However, it has been shown that, for polymers with side groups of either a high molecular weight or large degrees of asymmetry, the chain alignment effect on the thermal conductivity of electrosprun nanofibers has a tendency to be adversely impacted. As such, the heavy and complex side group of PVP (Figure 1b inset) renders the electrosprun nanofibers experiences little enhancement in thermal conductivity compared to the spin-coated films. The measured thermal conductivity of the PVP nanofibers is treated as the value for PVP in all calculations, no matter what form the polymer takes. This is reasonable even for nanometers-thick films, considering the phonon mean free path in PVP is only ~0.7 nm.

To explore the contact thermal resistance between AgNWs with a PVP interlayer, a small amount of AgNWs (Sigma–Aldrich, Lot No. 739448-25ML) were placed in a solution of 1% by weight PVP in ethanol. After remaining in solution overnight (~16 h), it was observed that the viscous polymer solution would adhere to the AgNW surfaces after removal and remain liquid for a sufficiently long time to form a meniscus between two AgNWs placed in contact (see the Supporting Information). By drop-casting the AgNW suspension onto a piece of polydimethylsiloxane (PDMS), individual nanowires could be identified and transferred to the thermal measurement device with a sharp probe mounted on an in-house built micromanipulator.

For the thermal measurement, a single PVP-coated AgNW with a length of >80 μm was identified and broken into three segments: one to serve as a continuous reference sample (Figure 2a) with the other two aligned to form a “contact sample” with a point contact between the suspended membranes (Figure 2b). Here, because of the pentagonal cross-section of the AgNWs, the hydraulic diameter is adopted (Dh = 4A/P, where A is the cross-sectional area and P is the perimeter) to represent the characteristic dimension of the wire, and the reported Dh is based on the silver core size without the PVP layer. Importantly, after thermal characterization, the contact samples were transferred to a piece of Si wafer, and focused ion beam (FIB) was used to cut the approximate center of the contact region, exposing the cross-section and allowing for estimation of the contact morphology (see the Supporting Information). The SEM micrograph of the cross-section at the contact is shown in Figure 2b.

Two sets of samples of 84 and 91 nm diameters, respectively, were measured, and the total thermal resistance of the contact and continuous wire samples is shown in Figure...
2c. From the cross-sectional view of the contact region, the PVP interlayer thicknesses are estimated as 4 nm for the 84-nm-diameter sample and 6 nm for the 91-nm-diameter sample. This suggests that the PVP layers on the individual wire are 2 and 3 nm thick, respectively. The samples were prepared within 1 h after the AgNW suspension was drop-cast on the PDMS, and because of the formation of the meniscus at the contact region, it is assumed that the PVP layers between the two AgNWs are fused together at the contact to form one layer of PVP.

Through careful probe operation, the suspended AgNW lengths between the two membranes for the continuous wire sample and the contact sample for each sample set were adjusted to be approximately the same. The measured total thermal resistance for these two samples can be expressed as

\[ R_{t,s} = R_M + R_{w,s} \]  
(1)

\[ R_{t,c} = R_M + R_{w,c} + R_c \]  
(2)

Here, \( R_{t,s} \) and \( R_{t,c} \) denote the measured total thermal resistance of the continuous wire and the contact sample, respectively. \( R_M \) is the total thermal resistance between the nanowire and the two suspended membranes. \( R_{w,s} \) and \( R_{w,c} \) represent the intrinsic resistance of the nanowire in the continuous wire and the contact sample, respectively. Finally, \( R_c \) is the resistance of the contact between the two nanowires, which can be further written as \( R_c = 2R_i + R_{PVP} \), where \( R_i \) is the interfacial thermal resistance between silver and PVP, while \( R_{PVP} \) denotes the thermal resistance of the PVP layer.

To extract \( R_c \) from the above equations, \( R_M \) is first considered. Recently, the thermal conductivity of individual, bare AgNWs of different diameters has been reported with careful confirmation that \( R_M \) is reduced to a negligible level. As such, the thermal conductivity of the bare AgNWs from that study can be treated as the intrinsic wire property. The measured thermal conductivity of PVP-coated AgNWs here is lower than the intrinsic value (see Figure S3 in the Supporting Information), and the difference can be attributed to the non-negligible \( R_M \) in the current measurement. Therefore, \( R_M \) can be solved based on eq 1 by calculating \( R_{w,s} \) with the intrinsic wire thermal conductivity. For the 84-nm sample, a bare AgNW of the same diameter has been previously measured, and \( R_M \) is estimated from eq 1 as \( 9.82 \times 10^5 \text{ K/W} \), or \( \sim 6\% \) of \( R_{t,s} \).

With non-negligible \( R_M \), it is important to ensure that the thermalization distance, i.e., the distance required for the nanowire to reach thermal equilibrium with the membrane, is shorter than the actual length the samples are contacting the suspended membranes. Based on a fin model, \( R_M \) can be written as

\[ R_M = \frac{2}{\sqrt{\ln K_A} \tan \left( \frac{L}{\sqrt{\ln A}} \right)} \]  
(3)
where \( h \) is the thermal conductance per unit area between the sample and the suspended membrane, \( w_c \) is the contact width, \( \kappa_s \) is the sample thermal conductivity, \( A_s \) is the sample cross-sectional area, and \( L_c \) is the contact length. Because \( \tanh(x) \) asymptotically approaches unity as \( x \) increases and already reaches a value of 0.964 for \( x = 2 \), it is reasonable to assume that a minimum thermalization distance, \( L_{c,\text{min}} \), can be estimated by the expression \( L_{c,\text{min}} = 2 \sqrt{\frac{\kappa_s}{\kappa_P}} \). The contact between the AgNW and suspended membranes occurs through one surface of the PVP-coated, pentagonal nanowire, with the 84-nm-diameter wire having a 2-mm-thick PVP layer. As such, the thermal conductance for the Ag-PVP/Pt composite interface can be estimated as \( h = \left( \frac{2 \kappa_{\text{PVP}}}{\kappa_{\text{PVP}}} + 2R_i^c \right)^{-1} \). Note that the thermal boundary resistances for unit area (\( R_i^c \)) at the PVP/silver and PVP/platinum interfaces are assumed to be approximately the same, which is reasonable, considering that electron–phonon coupling on the metal side dominates the interfacial thermal resistance. For the 84-nm sample, the minimum contact length is 3.37 \( \mu m \), which is beyond \( L_{c,\text{min}} \). Actually, \( R_i^c \) calculated from eq 3 is 9.75 \( \times \) 10\(^{-8} \) m\(^2\)-K/W, which compares very well with the 9.82 \( \times \) 10\(^{-8} \) m\(^2\)-K/W as previously derived using eq 1. Similar conclusions can be drawn for the 91-nm-diameter wire (see the Supporting Information).

The above analysis indicates that \( R_i^c \) is approximately the same for both the continuous wire and contact samples, allowing for extraction of \( R_i^c \) through subtracting eq 1 from eq 2. For the 84-nm sample, the lengths of the suspended AgNWs for the single wire and contact sample are both \( \sim 28 \mu m \), which leads to \( R_s = R_{i,c} - R_{i,c} \). However, for the 91-nm sample, the two AgNW segments in the contact sample are slightly longer than that of the continuous wire: 29 \( \mu m \) versus 27 \( \mu m \). In this case, \( R_{i,c} \) is scaled to account for the length difference and \( R_s = R_{i,c} - R_{i,c} \times 29 / 27 \). This inevitably introduces some error, because the scaling also applies to \( R_{i,c} \), however, since \( R_{i,c} \) for the 91-nm sample is \( \sim 13\% \) of the total resistance, the above approach only introduces a small error.

At 300 K, \( R_i^c \) is found to be 6.55 \( \times \) 10\(^6 \) K/W and 7.71 \( \times \) 10\(^6 \) K/W for the 84- and 91-nm samples, respectively. Interestingly, despite the presence of the PVP interlayer, these \( R_i^c \) values are lower than the \( \sim 1.3 \times 10^7 \) K/W value reported for the point contact between two 68-nm-diameter MWCNTs, which suggests silver nanowires could be more effective for enhancing the thermal conductivity of composites. To further understand thermal transport at the contact, the contact thermal resistance for unit area is calculated. At the contact, two flat, PVP-coated faces of the pentagonal AgNWs were observed to contact each other, as shown in the inset of Figure 2b, which leads to a parallelogram whose area (\( A_s \)) can be calculated with the expression \( A_s = \frac{w_c}{2} \sin \theta \), where \( w_c \) is the width of the contact surface and \( \theta \) is the contact angle. The contact angles were measured to be 55\(^\circ\) and 54\(^\circ\) for the 84- and 91-nm sample, respectively, with corresponding contact areas derived as 4107 nm\(^2\) and 4984 nm\(^2\), respectively. Thus, the area normalized contact thermal resistance (\( R_i^c \)) values at 300 K are 2.69 \( \times \) 10\(^{-8} \) m\(^2\)-K/W for the 84-nm sample and 3.84 \( \times \) 10\(^{-8} \) m\(^2\)-K/W for the 91-nm sample. Figure 2d also indicates that \( R_i^c \) decreases with temperature, which is largely determined by the lower PVP resistance as temperature escalates, as a result of the higher thermal conductivity of PVP at high temperatures. In addition, numerous studies have also shown the same trend for thermal boundary resistance, which could exist between silver and PVP.

As mentioned previously, \( R_i^c \) contains contributions from the PVP interlayer (\( R_{i,PVP} \)) and the interfacial thermal resistance between PVP and silver (\( R_i \)). For unit contact area, the resistance of the PVP layer can be solved by \( R_{i,PVP} = t / \kappa_{PVP} \), where \( t \) is the thickness, and \( R_i^c = (R_i^c - R_{i,PVP}) / 2 \), where a factor of 2 is introduced, since there are two PVP/silver interfaces. The derived \( R_i^c \) is shown in Figure 3a, and at 300 K, \( R_i^c \) assumes an average value of 5.50 \( \times \) 10\(^{-9} \) m\(^2\)-K/W. Note that, because the PVP interlayer thicknesses are approaching the SEM resolution, there is considerable uncertainty...
associated with the determination of $R''_i$ as indicated by the red-shaded region in Figure 3a. Nevertheless, the data are still able to shed light on aspects important to the design of polymer composites.

First, $R''_i$ for the AgNW-PVP-AgNW contacts is much higher than the $8.26 \times 10^{-11}$ m$^2$K/W recently reported for Ag/Ag interfaces. Moreover, despite the ~40 times larger contact area, $R_c$ for the PVP-coated AgNWs is still ~10 times higher than that reported for the contact between two 65-nm bare AgNWs (7.70 $\times$ 10$^{-13}$ K/W). This indicates that it is critical for AgNWs to reach direct contacts to most effectively enhance composite thermal conductivity.

Moreover, even when considering the upper bound of the uncertainty, the derived interfacial thermal resistance between PVP and silver, $R''_f$, is lower than the typical values ($\langle 1-8 \rangle \times 10^{-18}$ m$^2$K/W) for CNT–polymer systems, as reported in many studies. This difference in the thermal boundary resistance could contribute to an improved thermal conductivity enhancement with AgNWs. To demonstrate this, a generalized Maxwell–Garnett effective medium approximation (EMA) was adopted to predict the thermal conductivity enhancement of bulk PVP-AgNW composites against previously reported CNT–polymer composites for which the model was used to fit experimental data and determine the interfacial thermal resistance. According to the EMA, the thermal conductivity of a polymer composite with randomly dispersed, high-aspect-ratio rods can be described as:

$$\frac{\kappa_c}{\kappa_m} = \frac{3 + \varphi (\beta + \beta_l)}{3 - \varphi \beta_l}$$

with

$$\beta_l = \frac{2(\kappa_{t1} - \kappa_m)}{\kappa_{t1} + \kappa_m}, \beta_l = \frac{2}{\kappa_{t3} - \kappa_m} - 1$$

Here, $\kappa_c$ and $\kappa_m$ are the composite and polymer matrix thermal conductivities, respectively, and $\varphi$ is the volume fraction of nanoparticles. The parameters $\kappa_{t1}$ and $\kappa_{t3}$ are the equivalent nanofiller thermal conductivities along the transverse and longitudinal axes, respectively, when including the effects of thermal boundary resistance, according to

$$\kappa_{t1} = \frac{\kappa_t}{1 + \frac{2K_{s1}}{d}}, \kappa_{t3} = \frac{\kappa_t}{1 + \frac{2K_{s3}}{L}}$$

Here, $\kappa_t$ is the filler thermal conductivity, $d$ the nanofiller diameter, and $L$ the nanofiller length.

Figure 3b shows the predicted thermal conductivity enhancement ($\kappa_c/\kappa_m$) for a PVP–AgNW composite, compared against the corresponding values for SWCNT and MWCNT composites, as reproduced from the literature. Note that Maxwell–Garnett type EMA models consider “thermally isolated” filler networks, and while CNTs have been shown to electrically percolate at low volume fractions; no corresponding thermal percolation has been observed, which is consistent with the relatively large interfacial thermal resistance. Thus, the EMA model is considered valid at low volume fractions, and the linear profiles of thermal conductivity enhancement are consistent with enhancements observed for CNT–polymer composites.

Interestingly, despite the lower thermal conductivity for silver, the AgNW-PVP composites drastically outperform previously measured CNT composites, and as indicated by the red-shaded region in Figure 3b, the uncertainty associated with $R''_i$ only has a minor effect on their predicted thermal conductivity enhancement. Examination of the model parameters suggests that the larger $d$ and $L$ of AgNWs (84 nm and 80 $\mu$m, respectively) and the lower $R''_f$ correspond to higher equivalent filler thermal conductivities ($\kappa_{t1}$ and $\kappa_{t3}$), which renders AgNWs more effective nanofillers for thermal conductivity enhancement, when randomly dispersed in a polymer matrix.

In summary, the contact thermal resistance between individual AgNWs with a PVP interlayer was measured in order to understand thermal transport through polymer composites. The results indicate that the PVP layer leads to a significantly higher contact thermal resistance, compared to that between bare AgNWs, even though the contact area becomes much larger with PVP. A rather low interfacial thermal resistance between PVP and silver is derived, which, combined with the larger wire size, renders AgNWs much more effective nanofillers than CNTs for enhancement of the thermal conductivity of polymer composites.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01034. Sample preparation, measurement method, contact thermal resistance characterization, cross-sectional and contact area characterizations, and experimental uncertainty; effective medium approximation (EMA) model parameters (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Deyu Li — Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; Email: deyu.li@vanderbilt.edu

**Authors**

Matthew L. Fitzgerald — Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0001-8364-0924
Yang Zhao — Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0002-9103-2328
Zhiliang Pan — Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0001-8364-0924
Lin Yang — Department of Mechanical Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0002-6154-2765
Shihong Lin — Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0001-9832-9127
Godfrey Sauti — NASA Langley Research Center, Hampton, Virginia 23681-2199, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.nanolett.1c01034

### Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The authors thank the financial support from the U.S. National Science foundation (Award Nos. 1903645 and 1532107). M.L.F. acknowledges the graduate fellowship support from the National Aeronautics and Space Administration (No. NNCI-2025233). The work was performed in part at Cornell Nanoscale Facility, an NNCI member supported by NSF Grant No. NNCI-2025233.

REFERENCES