

Specifics of Thermal Transport in Graphene Composites: Effect of Lateral Dimensions of Graphene Fillers

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Cite This: <https://doi.org/10.1021/acsami.1c15346>



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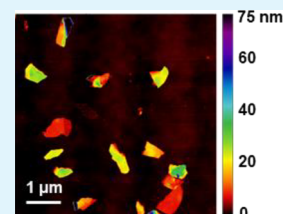
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ABSTRACT: We report on the investigation of thermal transport in noncured silicone composites with graphene fillers of different lateral dimensions. Graphene fillers are comprised of few-layer graphene flakes with lateral sizes in the range from 400 to 1200 nm and the number of atomic planes from 1 to ~100. The distribution of the lateral dimensions and thicknesses of graphene fillers has been determined via atomic force microscopy statistics. It was found that in the examined range of the lateral dimensions, the thermal conductivity of the composites increases with increasing size of the graphene fillers. The observed difference in thermal properties can be related to the average *gray* phonon mean free path in graphene, which has been estimated to be around ~800 nm at room temperature. The thermal contact resistance of composites with graphene fillers of 1200 nm lateral dimensions was also smaller than that of composites with graphene fillers of 400 nm lateral dimensions. The effects of the filler loading fraction and the filler size on the thermal conductivity of the composites were rationalized within the Kanari model. The obtained results are important for the optimization of graphene fillers for applications in thermal interface materials for heat removal from high-power-density electronics.

KEYWORDS: thermal conductivity, contact resistance, graphene, composites, thermal interface materials, power electronics



1. INTRODUCTION

The exfoliation and electrical experiments with graphene¹ motivated studies of other properties of this material, and led to the discovery of the unique thermal conductivity of graphene and few-layer graphene (FLG).^{2–6} In recent years, one can witness a transition of graphene and FLG to numerous practical applications, which utilize their thermal properties, including composite coatings, solid heat spreaders, and thermal interface materials (TIMs).^{7–21} The use of the graphene–FLG mixture as fillers in composites proved to be particularly beneficial. The initial studies found that the thermal conductivity of epoxy-based composites with low loading fractions of randomly distributed graphene fillers can be improved substantially by a factor of $\times 25$.^{7,22} A similar significant enhancement in the thermal conductivity characteristics of noncured TIMs with graphene fillers has been reported by some of us and others.^{14,17,23,24} A comparative study of the thermal conductivity of graphene-based noncured TIMs with commercially available TIMs demonstrated that the TIMs with graphene conduct heat more effectively even with lower filler loadings.¹⁴ Reports from different research groups confirmed the potential of graphene fillers for thermal management applications (for comprehensive reviews on the topic, see refs 25, 27). There is a general consensus that unique heat conduction properties of single-layer graphene (SLG) and FLG are the enablers of such applications.^{2,6} Here and below, we adopt a convention that, in the thermal context, the term “graphene fillers” means a blend of SLG and FLG.

Many studies on TIMs with graphene fillers are focused on the thermal conductivity and thermal diffusivity values of the resulting composites as a function of the graphene loading fraction.^{25–27} Several studies addressed the issues of the thermal percolation threshold^{15,28} and “synergistic” effects.^{12,29–32} In the context of various TIMs, it was established that the percolation threshold depends on the filler size.^{33–35} The existence and the strength of the “synergistic” effect, *i.e.*, the additional enhancement of the thermal conductivity when a single type of filler with different sizes or two or more filler materials are used, is also known to depend on the size and aspect ratio of the fillers. Despite the importance of the knowledge of how the lateral dimensions of graphene fillers affect the thermal conductivity of the composites, there have been a limited number of studies on this subject.^{28,36,37} We are not aware of any reports on the effect of the graphene filler size on the thermal contact resistance of TIMs at the interfaces with solid surfaces. Possible reasons for the lack of such data are the challenges in the preparation of a consistent set of samples with different and quantifiable average lateral size of fillers when prepared in large quantities required for TIM preparations.

Received: August 11, 2021

Accepted: October 13, 2021

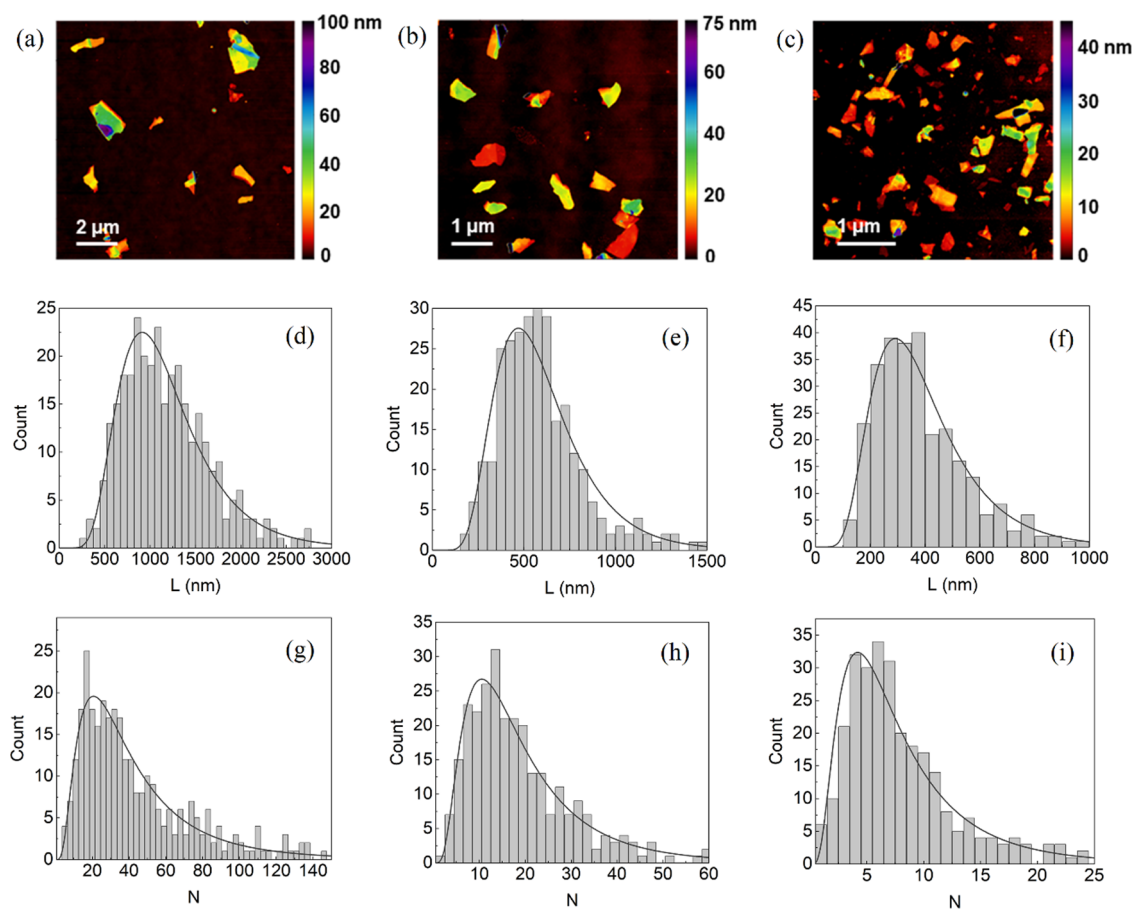


Figure 1. Characterization of lateral dimensions of graphene fillers. (a–c) AFM images of the large (1200 nm), medium (800 nm), and small (400 nm) size fillers, respectively after drop-casting the dispersions on Si/SiO₂. (d–f) Histograms of the measured filler lengths used for determining three groups of the filler sizes. (g–i) Histograms of the number of atomic planes in the three groups of the fillers. Note that the large fillers have lateral dimensions near or exceeding the gray phonon MFP in graphene.

Investigation of thermal transport properties of composites with graphene and FLG fillers that have different lateral dimensions is important for both industrial applications and fundamental science. We hypothesize that graphene fillers with lateral dimensions exceeding the phonon mean free path (MFP) preserve their high intrinsic thermal properties by limiting the effect of phonon–edge scattering. On the other side, the fillers with excessively large lateral dimensions can be technologically impractical owing to the strong bending of the fillers and increased bond line thickness (BLT). There are other factors, related to the lateral size of the fillers, which can affect the heat conduction in the composites. They include the Kapitza resistance between the fillers and matrix material,³⁸ the specific surface area, the interface area between the filler and matrix,^{39–43} and the defect density.^{4,44–46} The above considerations motivated us to investigate the specifics of heat conduction in TIMs with graphene fillers where the lateral dimensions of the fillers are below, close, or above graphene’s gray phonon MFP. A particular emphasis of the study was on selecting a proper sample set with the well-defined average lateral dimensions of the fillers, systematic analysis of the filler size distribution, and accurate thermal measurements following the standard techniques used in industry for TIM performance characterization. In order to understand the effect of the filler size, we intentionally used a low loading of the graphene fillers, kept the dimensions as uniform as possible, and selected the lateral dimensions of the fillers to be relatively small, *i.e.*, close

to the gray phonon MFP. For the above reasons, the resulting values of the thermal conductivity of the studied composites were not high. Thermal transport across the interface between the composite and the solid surface was another component of this research. The latter has practical importance for the application of graphene TIMs for the thermal management of power electronics.

2. EXPERIMENTAL PROCEDURES

In this study, different sets of noncured TIMs with the base polymer of silicone oil and inclusions of graphene and FLG fillers were prepared. The fillers were produced from graphite using the liquid phase exfoliation (LPE) technique^{47–51} in aqueous surfactant solution in combination with liquid cascade centrifugation^{52,53} for size selection. This allowed us to produce three fractions from the same stock dispersion with different lateral size and thickness distributions. The exfoliated graphene fillers were extracted from the solvent and incorporated within the base polymer to produce the required composites. The details of the exfoliation and composite preparation are outlined in METHODS. The fillers were characterized for lateral dimension and thickness, *i.e.*, number of layers, using atomic force microscopy (AFM) and optical extinction spectroscopy to assess the concentration/mass. In Figure 1, we present the AFM characterization data for the three size-selected sets of fillers. Figure 1a–c shows the two-dimensional images of the dispersed graphene fillers in the size-selected fractions. The procedure used to assess the average dimensions is outlined in METHODS. The resultant histograms for the longest dimension of the fillers (termed length, *L*) are given in Figure 1d–f while the histograms for the number of atomic planes, *N*,

are given in Figure 1g–i. Note that because of the lognormal shape of the distributions, there are different ways to describe the average. Here, we focus on the arithmetic mean of the filler's longest lateral dimension, $\langle L \rangle$, which was calculated to be 1200, 800, and 400 nm for the three samples, and the average number of atomic planes, $\langle N \rangle$, which was determined to be 40, 19, and 8. For simplicity, we label these fillers as “large,” “medium,” and “small,” respectively. Additional characterization data for the graphene fillers, *i.e.*, scanning electron microscopy (SEM) and optical extinction spectroscopy, are provided in the Supplementary Information.

It is important to note that there exists a specific correlation between the number of atomic planes in FLG and its lateral dimensions. One cannot obtain FLG fillers with a fixed number of atomic planes and different lateral dimensions. This is related to details of the exfoliation mechanism which can be understood in terms of delamination accompanied by tearing.⁵⁴ The centrifugation, which is required for the size selection, enhances this correlation and typically produces small fillers that are thinner and large fillers that are thicker.^{52–54} This correlation can be illustrated via a plot of the filler area as a function of the number of the atomic planes. Figure 2a shows

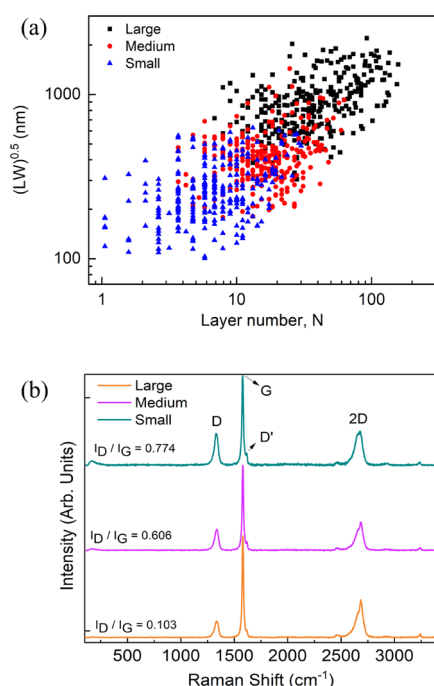


Figure 2. (a) Correlation between the measure of the lateral dimensions of the fillers and the number of the atomic planes. Numerous data points denote the multiple measurements conducted with AFM. (b) Raman spectra of the graphene fillers of different lateral dimensions.

the measure of the characteristic lateral length, $L_* = (L \times W)^{0.5}$ versus the number of atomic planes, N (here L and W are the measured “length” and “width” of the fillers from AFM). In this plot, each data point corresponds to a single graphene sheet measured with AFM in the size-selected fractions. The exact specification of the fillers obtained from AFM data is summarized in Table 1. For FLG, the lateral dimensions affect the thermal transport stronger than the thickness.^{25–27,55–60} For this reason, the synthesized three sets of composite samples are meaningful for understanding the specifics of heat conduction and the effects of the filler size.

We have verified the quality of fillers using Raman spectroscopy (Renishaw inVia). Figure 2b shows the measured Raman spectra of the size-selected graphene samples used in this study. To conduct the tests, a small portion of the fillers were transferred onto a Si/SiO₂ substrate. The light scattering spectra were collected under laser excitation of the wavelength 633 nm (red) and an excitation power of

Table 1. Characteristics of Graphene–FLG Fillers

	symbol	large	medium	small
Average length (nm)	$\langle L \rangle$	1200	800	400
Aspect ratio (length/width)	$\langle L/W \rangle$	1.8	2.1	2.3
Aspect ratio (length/thickness)	$\langle L/t \rangle$	110	120	200
Average layer number	$\langle N \rangle$	40	19	8
Characteristic length $(L \times W)^{0.5}$ (nm)	$\langle L_* \rangle$	900	430	270

2 mW at room temperature. The Raman spectra show the well-known signatures of FLG, which are the G peak and 2D band.^{53,56,57,61–63} As expected, the intensity of the disorder D peak increases as the size of the fillers decreases. The evolution of the peaks with the lateral dimensions and the number of atomic planes is in line with prior literature reports.^{61,62,64–66} The I_D/I_G ratio is correlated with the difference in the average size of the fillers.⁶⁷ The I_D/I_G ratio decreases as the size of the fillers increases, changing from 0.774 for the small fillers to 0.103 for the large fillers. The evolution of the D peak and I_D/I_G can be explained by the relaxation of the selection rules, which prohibit the appearance of the D peak in graphene with perfect translation symmetry, without defects or edges.^{68,69} In the samples with smaller graphene fillers, the excitation laser light covers more graphene fillers with the edges that act as inherent defects thus resulting in an increased I_D/I_G ratio. The 2D peak becomes more symmetric with decreasing dimensions of the fillers which is in this case related to a change in the number of atomic planes. However, as outlined recently, this cannot be used as a quantitative measure for thickness in LPE graphene.⁷⁰ A comparison of the I_D/I_G ratios with the AFM acquired characteristics of the graphene fillers is presented in the Supplementary Information.

The total thermal resistance, R_{tot} , bulk thermal conductivity, and the thermal contact resistance, R_C , of the TIMs with the steel plates were measured using an industrial TIM tester (LongWin Science and Technology Corp.). The instrument operates based on the procedures and regulations described in the standard ASTM D5470.⁷¹ The prepared TIMs were tested for their thermal properties by applying TIMs between two finely polished steel plates, with the roughness in the nm-scale range. The two plates are the heat source and heat sink. The thermal performance of the TIM at the interface is tested by measuring the heat flow from the source to the heat sink and the temperature gradient across the TIM layer.¹⁷ Assuming a one-dimensional heat flow, the apparent thermal conductivity of the TIMs can be calculated by solving the one-dimensional Fourier heat transport equation. The total thermal resistance from our measurements can be defined as:^{7,72,73}

$$R_{\text{tot}} = \frac{BLT}{K_{\text{TIM}}} + R_{C1} + R_{C2} \quad (1)$$

where K_{TIM} , R_{C1} , and R_{C2} are the thermal conductivity of the TIM and the thermal contact resistances of the TIM with the two plates present in the measurement equipment, respectively. The measurements were carried out on TIMs with graphene of three filler sizes at multiple loading fractions. All measurements have been performed under an applied pressure of $P = 0.55$ MPa (~ 80 psi). Further details of the thermal testing are provided in METHODS.

3. RESULTS AND DISCUSSION

The total thermal resistance, R_{tot} of the prepared noncured graphene composites as a function of BLT is presented in Figure 3a–c. The data are shown for all three lateral dimensions of the graphene fillers at different loading fractions, f . The acquired data were fitted using the least-squares linear regression line at each loading fraction and for each size of graphene fillers. The bulk thermal conductivity of each TIM was then obtained from the inverse of the regression line slope, K_{TIM} ($\text{Wm}^{-1} \text{K}^{-1}$) = $(1/\text{Slope}) \times 100$. The total thermal

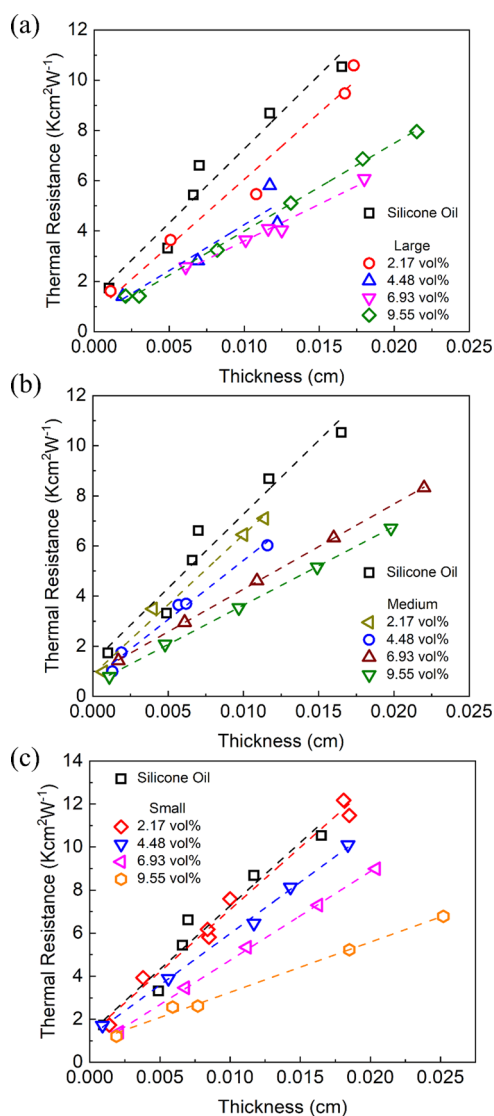


Figure 3. Total thermal resistance of the TIMs with (a) large, (b) medium, and (c) small graphene fillers as a function of the TIM's BLT. The slope and y -intercept of the fitted dashed lines were used to calculate the thermal conductivity and thermal contact resistance of each set.

contact resistance, $2R_C$, assuming that $R_{C1} = R_{C2} = R_C$ was acquired from the y -intercepts of the fittings. One can see that the total thermal resistance at constant thickness is the highest for the pure matrix material, i.e., silicone oil. The addition of graphene to silicone oil reduces the total thermal resistance significantly. However, it is difficult to make any conclusions about the effect of the filler size from this plot. The latter can be done in a meaningful way from the analysis of the thermal conductivity and thermal contact resistance.

Figure 4 shows the thermal contact resistance, R_C , as a function of the graphene loading fraction for three examined graphene filler sizes. The thermal contact resistance is the smallest for the graphene fillers with the largest lateral dimensions. As seen, R_C decreases with increasing filler loading fraction. The dependence of the thermal contact resistance on the filler loading and lateral dimensions can be interpreted with the help of the following semiempirical model:^{74,75}

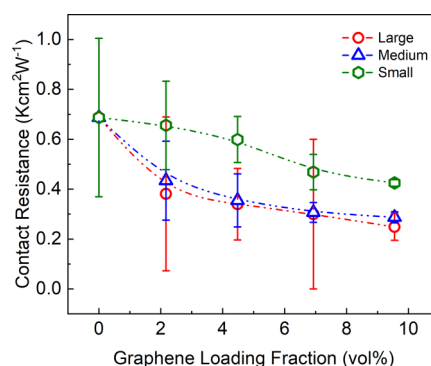


Figure 4. Contact resistance of the TIMs as a function of the graphene filler loading fraction. Error bars show the standard associated with the linear regressions over experimental data. Dashed lines are shown as guides to the eye.

$$R_{C1+C2} = 2R_C = c \left(\frac{\zeta}{K_{TIM}} \right) \left(\frac{G}{P} \right)^n \quad (2)$$

In eq 2, $G = \sqrt{G'^2 + G''^2}$ is a function of the storage (G') and loss shear modulus (G'') of the TIM. The parameters ζ and P are the surface roughness of the binding steel plates and the applied pressure on the sample during the measurements. c and n are empirical coefficients. There are two competing parameters, K_{TIM} and G , in this equation, as more fillers are introduced to the base polymer. Both parameters, irrespective of the size of the fillers, increase with the addition of fillers. However, G' and G'' strongly depend on the filler size. At constant filler loading, the smaller the filler size, the higher the values of G' and G'' and thus, G .^{76–83} For this reason (see Figure 4), with a constant ζ and P , the smaller graphene fillers exhibit the highest thermal contact resistance. It is worth noting that the rheological properties of noncured TIMs and their variation with pressure and temperature have important implications in practical applications mostly related to pump-out issues.^{14,84–86} It is generally suggested that in order to avoid the issue of pump-out, G' of noncured TIMs should be greater than G'' .⁷³

In Figure 5, the symbols show the extracted experimental thermal conductivity as a function of the graphene loading fraction for three examined graphene filler sizes and its comparison with theoretical modeling (dashed lines). The measured thermal conductivity of the base polymer matrix–

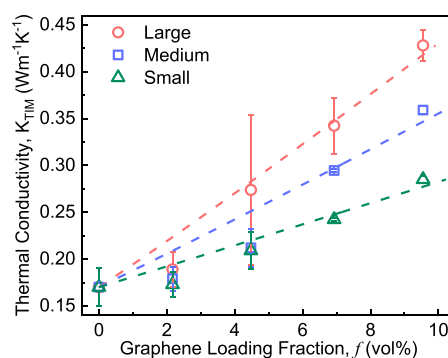


Figure 5. Experimentally acquired thermal conductivity (symbols) of the noncured TIMs as a function of the graphene loading fraction, f , for three different sizes of the fillers with comparison to the Kanari model (dashed lines).

Table 2. Parameters of the Kanari Model for Graphene Composites

filler type	layer number (N)	thickness (a_1)[nm]	plane dimension ($a_2 = a_3 = L_s$)[nm]	φ [rad]	M	B
large	40	14	900	1.5552	0.0164	81.5419
medium	19	6.65	430	1.55533	0.0163	82.0100
small	8	2.8	270	1.56043	0.0110	121.5660

silicone oil was $0.17 \text{ Wm}^{-1} \text{ K}^{-1}$ which agrees with the previously reported values.^{17,87–89} The thermal conductivity is higher for the large filler size TIMs at all the measured loading fractions. We rationalize this trend by comparing the size of the graphene fillers with the average, also referred to as *gray* phonon MFP in graphene. The gray phonon MFP in graphene is reported to be $\sim 800 \text{ nm}$ at RT.^{55–60,90} The improvement in the thermal conductivity of the TIMs originates from the partial contribution of thermal transport via the graphene fillers. If the filler lateral dimensions become smaller than the phonon MFP, its intrinsic thermal conductivity decreases. The simple estimate comes from the Debye model, where the thermal conductivity $K \sim C\nu\Lambda$ (here, C is the volumetric specific heat, ν is the average phonon group velocity, and Λ is the average phonon MFP). When the size of the filler $L < \Lambda$, the thermal conductivity, K , scales down linearly with lateral dimension, L . This explanation remains valid for the thermal transport regime below and above the thermal percolation threshold.¹⁵

One should also note that the measured values of thermal conductivity of the examined TIMs are not high. The goal of the present study was not to achieve the highest thermal conductivity but rather a systematic study of the effect of the filler size on TIM's thermal transport characteristics. For this reason, we used a low loading of graphene fillers, which allowed us to avoid agglomeration and viscosity increase, the relatively small size of the fillers, close to the gray phonon MFP, and the fillers of the same size within each batch. In order to obtain the highest possible values of the thermal conductivity with graphene fillers, one would need to use higher loading fractions of the fillers, select the fillers with larger average lateral dimensions, prepare a mixture of fillers with different sizes to achieve the synergistic effect, and functionalize the fillers for better coupling to the matrix. We have reported strategies for maximizing the enhancement of the thermal conductivity of graphene curing and noncuring composites and TIMs elsewhere.^{12,14,15} One should note that the low loading of graphene fillers with the noncuring base material allowed us to minimize the problems associated with the high viscosity of composites at higher loadings. The viscosity of the composites depends on the filler loading and filler size distribution. The viscosity also affects the "pump-out" in noncured TIMs. These secondary effects go beyond the scope of the present work and will be addressed in a separate study.

We employed the theoretical model of Kanari⁹¹ to investigate the effect of the filler content and its characteristic dimensions on the thermal conductivity of the polymer TIMs as shown in Figure 5. This model was originally introduced as an empirical extension of the Bruggeman relation.⁹² The derivation of the Kanari model within the micromechanical framework was described in detail previously.⁹³ According to this approach, the thermal conductivity, K_{TIM} , of a composite consisting of a polymer matrix laden with particles of an arbitrary shape is determined by the equation:

$$\frac{k_f - K_{\text{TIM}}}{k_f - k_m} \left(\frac{k_m}{K_{\text{TIM}}} \right)^{1/B} = 1 - f \quad (3)$$

in which k_m and k_f are the thermal conductivities of the matrix and filler, respectively, f is the filler volume fraction, and B is a parameter characterizing shape of the filler particles. We treat these inclusions (stacks of graphene plates) as oblate ellipsoids of rotation with semiaxes $a_1 < a_2 = a_3$, where a_1 denotes the characteristic thickness of a stack, and $a_2 = a_3 = \langle L_s \rangle$ stands for its average characteristic in-plane size. Under this condition and given that $k_f \gg k_m$, the coefficient B reads

$$B = \frac{4 - 3M}{3M(1 - M)} \quad (4)$$

with

$$M = \frac{2\varphi - \sin \varphi}{2\sin^2 \varphi} \cos \varphi, \quad \cos \varphi = \frac{a_1}{a_2} \quad (5)$$

Figure 5 shows reasonable agreement between the experimental data of composites with stacks of small, medium, and large graphene fillers and predictions of eq 3. Each set of data is matched separately by means of the only parameter: the effective thermal conductivity of stacks, k_f . In simulation, we adopt the value $k_m = 0.17 \text{ Wm}^{-1} \text{ K}^{-1}$ for the thermal conductivity of the matrix. The coefficients φ , M , and B , related to the aspect ratio of stacks, are calculated based on the experimental characterization of the fillers (Table 1) and their values are summarized in Table 2. The experimentally obtained set of data for TIMs with large, medium, and small size graphene fillers has been presented in the supplementary document.

The effect of the in-plane size of fillers on their effective thermal conductivity, k_f , is illustrated in Figure 6. In this figure, k_f is plotted versus L_s together with the approximation of the data by an exponential function:

$$k_f = k_f^0 + k_f^1 \exp(-\alpha L_s) \quad (6)$$

where $k_f^0 = 3.32$, $k_f^1 = -4.83$, and $\alpha = 0.0033$ are fitting parameters. Figure 6 shows that k_f increases by a factor of 2.2

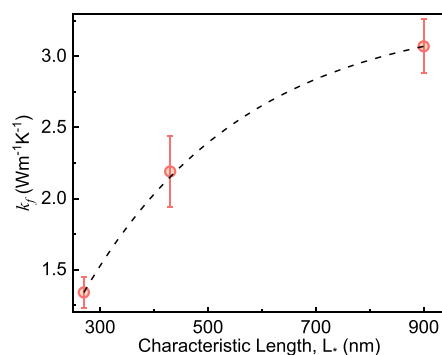


Figure 6. Effective thermal conductivity of filler k_f versus the average characteristic in-plane size of graphene fillers $\langle L_s \rangle$.

with $\langle L_s \rangle$ when the in-plane size of the fillers grows from 270 to 900 nm. The extracted effective thermal conductivity of fillers is orders of magnitude smaller than the intrinsic thermal conductivity of graphene because of the filler–polymer thermal boundary resistance. However, the decrease in the effective thermal conductivity of the fillers as their size shrinks below graphene's phonon MFP is originated from a strong suppression of its intrinsic thermal conductivity because of the enhanced phonon–edge scattering.

Our present detailed systematic study proves that a stronger enhancement of the thermal conductivity of graphene composites can be achieved when the fillers with larger lateral dimensions are used. This conclusion is in line with our own early observation,⁹⁴ and a few other reports that were performed with different graphene filler sizes.^{28,36,37,95,96} The prior studies were focused on substantially larger fillers, with dimensions typically above 5 μm . In many cases, no accurate assessment and averaging were performed for the size distribution of the fillers. By selecting the average filler sizes near the phonon MFP in graphene, i.e., slightly smaller, almost equal to MFP, and slightly larger, we were able to connect the observed trend with the intrinsic heat conduction properties of FLG. The observation that the thermal contact resistance also decreases with increasing the graphene filler size is not obvious, and to some degree, it is counter-intuitive. The obtained trends shed light on the specifics of heat conduction in graphene composites and can be used for the optimization of graphene TIMs for practical applications.

4. CONCLUSIONS

We reported on the thermal properties of noncured silicone composites with graphene fillers of different lateral dimensions. To elucidate the effect of the physical size of graphene fillers, we intentionally used a low loading of graphene fillers to avoid agglomeration, used relatively small fillers, and kept the size uniform as much as possible. The studied graphene fillers were comprised of FLG flakes with lateral sizes in the range from 400 to 1200 nm and the number of atomic planes from one to ~ 100 . The physical characteristics of the graphene fillers were determined with AFM and verified with various characterization techniques. It was found that in the examined range of the lateral dimensions, the thermal conductivity of the composites increases with increasing size of the graphene fillers. The thermal contact resistance of composites with graphene fillers of 1200 nm lateral dimensions was also smaller than that of composites with graphene fillers of 400 nm lateral dimensions. The effects of the filler loading fraction and the filler size on the thermal conductivity of the composites were rationalized within the Kanari model. The obtained results are important for the optimization of graphene fillers for applications in TIMs for heat removal from high-power-density electronics where the thermal resistance between the device and packaging is often a bottleneck impeding the heat removal. The high-power switches implemented with diamond and other wide bandgap semiconductors are also often characterized by higher roughness on the surface allowing for the use of TIMs with larger fillers for enhanced performance.

5. METHODS

5.1. Liquid Phase Exfoliation. The preparation of graphene dispersions was achieved by probe sonication of the commercially acquired graphite powder (Sigma Aldrich 496596) in an aqueous solution of sodium cholate with an initial concentration of 40 g L^{-1} .

The obtained powder was immersed in 80 mL of aqueous surfactant solution ($C_{\text{surf}} = 6 \text{ g L}^{-1}$) in a stainless-steel beaker and then subjected to a two-step sonication process. The first step was carried out to remove the impurities present in the powder. (1) The mixture was sonicated for a duration of 1 h at a 60% Amplitude in a 8 s on, 2 s off pulse sequence, with a Sonics Vibracell VCX 500 (500 W), equipped with both a threaded probe and a replaceable tip. The dispersion was kept at 5 $^{\circ}\text{C}$ in a cryostat cooled water bath to avoid heating of the sample during the process of sonication. After the completion of the sonication process, the dispersion was centrifuged at 3800g for 1.5 h in a Hettich Mikro 220R centrifuge, equipped with a 1016 fixed-angle rotor at a temperature of 15 $^{\circ}\text{C}$. The supernatant containing the water-soluble impurities was discarded and the sediment was re-dispersed in 80 mL of 2 g L^{-1} aqueous surfactant solution. (2) This dispersion was then again sonicated for 5 h at a 60% Amplitude in a 6 s on, 2 s off pulse sequence.

In order to separate the acquired nanosheets by their size, we utilized the technique of liquid cascade centrifugation with sequentially increasing the rotation speeds (2 h each step, with a temperature of 15 $^{\circ}\text{C}$). After each centrifugation step, the supernatant and sediment were separated, the sediment was collected in reduced volume ($\sim 10 \text{ mL}$) and surfactant concentration (0.1 g L^{-1}), and the supernatant was subjected to centrifugation at higher speeds. Here, the relative centrifugal field (RCF) in units of the Earth's gravitational force, g , is used to describe the centrifugation conditions. Centrifugation was performed with a JA25.50 fixed-angle rotor of a Beckman Coulter Avanti centrifuge at a temperature of 15 $^{\circ}\text{C}$ for 2 h with 50 mL centrifuge tubes (VWR, order number 525-0402) filled with 20 mL of each dispersion. The following RCFs were used: 30, 200, and 2500g. The supernatant after 2500g was discarded. The sediment after the centrifugation step at 30g contains the largest sheets, but also unexfoliated bulk material. To separate the two, the dispersion was left to settle for 16 h and the top 80% of the volume was decanted and collected. This sample is denoted as "large." "Medium" refers to the sample trapped between 30 and 200g centrifugation, while "small" denotes the sample obtained from centrifugation between 200 and 2500g. The exfoliation and size selection procedure were repeated four times to produce a sufficiently large mass of nanosheets. The same fractions of all batches were combined. In a final step, the filler was transferred to *t*-butoxymethyl-oxirane as a solvent for better compatibility with the composite preparation. To this end, the combined fractions were centrifuged at 3000g for 2 h, the clear supernatant was removed, and the sediment was re-dispersed in the solvent.

5.2. Characterization of Fillers. Optical extinction of the fillers was measured on a Varian Cary 6000i in quartz cuvettes with a pathlength of 1 cm in 0.5 nm increments and an integration time of 0.1 s/nm. The obtained sediments after liquid cascade centrifugation (LCC) were diluted with an aqueous surfactant solution containing (0.1 g L^{-1}) such that their optical densities after background subtraction were < 1 . The extinction at 750 nm was multiplied with the dilution factor and the concentration determined using the reported size-independent extinction coefficient of 54.5 $\text{g L}^{-1} \text{ cm}^{-1}$.⁵³ With knowledge of the total volume, the total mass of graphene in each sample was calculated. For AFM, the concentrated dispersions after size selection were diluted with de-ionized water to optical densities of ~ 1 and drop-cast on Si/SiO₂ wafers that were heated to $\sim 150 \text{ }^{\circ}\text{C}$ on a hotplate. This results in flash evaporation of the solvent to minimize aggregation on the substrate. For imaging, an aluminum coated silicon AFM cantilever and tip (OLTESPA-R3) was used with the Dimension ICON3 scanning probe microscope (Bruker AXS S.A.S.) in ScanAsyst mode (noncontact) in air under ambient conditions. Typical image sizes ranged from $20 \times 20 \mu\text{m}^2$ in the case of the largest sheets to $5 \times 5 \mu\text{m}^2$ for the sample containing the smaller sheets. The scanning parameters used were a pixel of 1024 lines with a scan rate of $\sim 0.4 \text{ Hz}$ and a peak force setpoints of $\sim 0.1 \text{ V}$. Using Gwyddion software, the longest dimension (length), dimension perpendicular (width), and thickness of ~ 300 individually deposited nanosheets in each sample were manually measured. The measured apparent thickness was essential to obtain the layer number which was

acquired using the previously reported step height of LPE graphene of 0.9 nm.⁹⁷ The lateral dimensions were corrected for cantilever broadening and pixilation by using an empirical correction.⁹⁸ From the distributions, the arithmetic averages of the dimensions were calculated. Because of the lognormal shape of the distributions, we note that the arithmetic average is larger than the maximum (i.e., the mode) of the distribution. To estimate the average length/thickness aspect ratio, the length of each sheet was divided by the layer number multiplied with the crystallographic thickness of one layer (0.35 nm) and the arithmetic mean calculated.

5.3. Composite Synthesis. The exfoliated graphene fillers were centrifuged with a solvent of *t*-butoxymethyl-oxirane in a vial at 7000 rpm for 2 min to ensure that the fillers were visually separated from the solvent. The solvent was removed from the vial to an extent using a dropper and the remaining contents of the vial were transferred to a petri dish in a fume hood for 24 h at room temperature. This enabled the solvent to completely evaporate leaving us with only the fillers. These extracted fillers were precalculated and added to the base polymer matrix of silicone oil (Fisher Scientific, USA), also known as PDMS—poly(dimethylsiloxane). The obtained compound was then shear mixed (Flacktek Inc.) at a speed of 2000 rpm for 10 min followed by a speed of 3000 rpm for 15 min to ensure the homogenous distribution of the filler in the polymer. This process was repeated for all the filler sizes and with all loading fractions.

5.4. Thermal Characterization. The prepared composites were experimentally tested to acquire their thermal conductivity and contact resistance with the LW-9389 industrial ASTM-D5470 LongWin TIM tester (LongWin Science and Technology Corp, Taiwan). Experimental parameters with a pressure of 80 psi and temperature of 80 °C for a duration of 40 min for each data point were used for the noncured composites with graphene fillers.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c15346>.

SEM and Raman results of the exfoliated graphene filler and its optical extinction characterizations and additional data on the mass density of the synthesized composites (PDF)

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Author Contributions

F.K. and A.A.B. conceived the idea of the study and coordinated the project. S.S. prepared the thermal compounds, performed thermal conductivity measurements, thermal contact resistance measurements, and conducted data analysis of thermal and Raman data; F.R. performed LPE, AFM, and optical extinction measurements on the fillers and conducted analysis; D.W. assisted with thermal measurements and analysis; Z.B. performed Raman spectroscopy measurements and assisted in thermal compound preparation and analysis of Raman data; A.D.D. performed modeling of the experimental data and compared them; F.K. contributed to the experimental and theoretical data analysis; S.B. performed SEM of the graphene fillers; C.B. supervised LPE, AFM, and optical absorption of the fillers and contributed to analysis; A.A.B. contributed to thermal and Raman data analyses; F.K. and A.A.B. led the manuscript preparation. All authors contributed to writing and editing of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work at UC Riverside was supported, in part, by ULTRA, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0021230.

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