Electronic Supplementary Material (ESI) for RSC Advances.

Multi-scale hybrid spherical graphite composites：a lightweight thermal interface material with high thermal conductivity and simple processing technology

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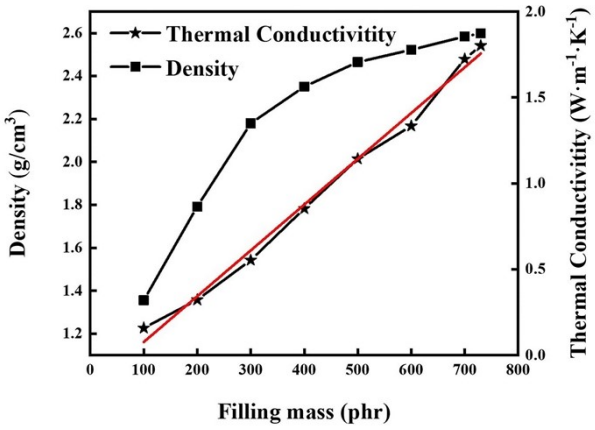

Fig. S1. The thermal conductivity and density of the Al_2O_3 filled composites under different filling contents.

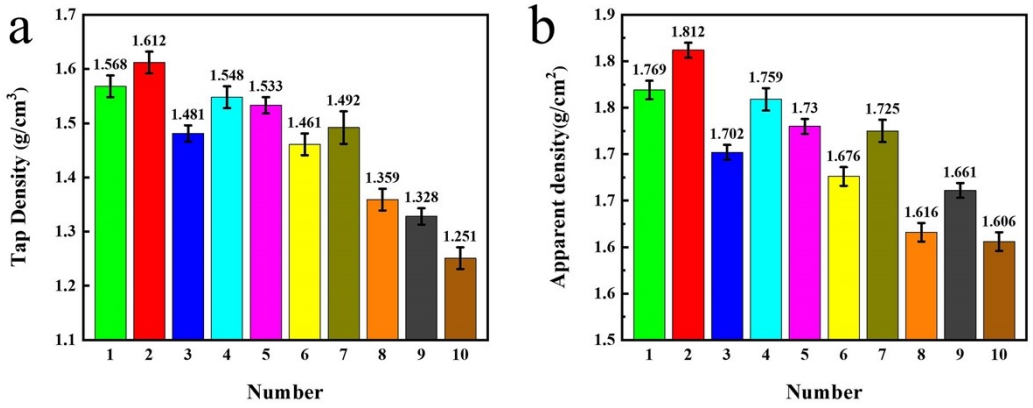

Fig. S2. (a) The tap density of graphite powders from formulations No. 1 - No. 10, (b) the apparent density of No. 1 - No. 10 composites.

Table S1

The specific percentage ratio of G-31, G-13 and G-3 in different formulations

number	Mass fraction/%		
	G-31	G-13	G-3
1	31	46	23
2	45	28	27
3	25	60	15
4	55	30	15
5	50	10	40
6	20	40	40
7	20	20	60
8	100	0	0
9	0	100	0
10	0	0	100

Appendix S1: Detailed computing process of calculation method No. 2

Step 1: Data processing.

Mostly，the particle size distribution of powders conforms to lognormal distribution, which meets the following relationship

$$p_{\mu,\sigma(x)} = \begin{cases} \frac{1}{\sqrt{2\pi}\sigma x} e^{-\frac{(lnx-\mu)^2}{2\sigma^2}}, & x > 0' \\ 0, & x \leq 0. \end{cases} \quad (1)$$

where μ and σ are the parameters which need to be regressed. In the experiment, the cumulative volume frequency curve of the corresponding particle size can be obtained directly by using the laser particle size analyzer. However, the parameters μ and σ in the distribution are usually not obtained directly.

Here, it is not recommended to directly call the parameter regression of lognormal distribution function for particle size distribution through Origin or MATLAB software. The raw data of the m-th kind of powder obtained by laser particle size analyzer is volume fraction $\{x_i^{(m)}\}_{i=1}^{n}$ in particle diameter intervals $\{[D_i^{(m)},D_{i+1}^{(m)}]\}_{i=0}^{n}$. While the distribution of $\{x_i^{(m)}\}_{i=1}^{n}$ is not uneven so direct calculation will cause large deviation. We perform nonlinear least squares regression about $\{\mu_m\}_{m=1}^{k}$, $\{\sigma_m\}_{m=1}^{k}$ on the volume fraction $\{x_i^{(m)}\}_{i=1}^{n}$ as below:

$$min_{\mu,\sigma}\frac{1}{2}\sum_{i=1}^{n}\left[\int_{D_i^{(m)}}^{D_{i+1}^{(m)}} p_{\mu,\sigma}(x)dx - x_i^{(m)}\right]^2. \tag{2}$$

Denote

$$F_i(\mu,\sigma) = \int_{D_i^{(m)}}^{D_{i+1}^{(m)}} p_{\mu,\sigma}(x)dx - x_i^{(m)}, i = 1,2,\cdots,n. \tag{3}$$

Then, Eq. 2 it is equivalent to the following form:

$$min_{\mu,\sigma} f(\mu,\sigma) \triangleq \frac{1}{2}\|F(\mu,\sigma)\|^2. \tag{4}$$

where $F(\mu,\sigma) = (F_1(\mu,\sigma),F_2(\mu,\sigma),...,F_n(\mu,\sigma))$. Here, we solve parameters $\{\mu_m\}_{m=1}^{k}$ and $\{\sigma_m\}_{m=1}^{k}$ by Levenberg Marquardt method.

The derivation of Levenberg Marquardt method for Eq. 4 are as follows:

$$\nabla F(\mu,\sigma) = \left(\frac{\partial F}{\partial \mu}, \frac{\partial F}{\partial \sigma}\right) \tag{5}$$

where $\frac{\partial F}{\partial \mu}$ and $\frac{\partial F}{\partial \sigma}$ are both $n \times 1$ vector. When calculating the parameters of the m-th powder ($m = 1, 2, \ldots, k$), for the i-th data ($i = 1, 2, \ldots, n$),

$$\begin{aligned} \frac{\partial F_i}{\partial \mu}(\mu,\sigma) &= \frac{\partial}{\partial \mu}\left[\int_{D_i^{(m)}}^{D_{i+1}^{(m)}} \frac{1}{\sqrt{2\pi}\sigma x} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}} dx - x_i^{(m)}\right] \\ &= \frac{\partial}{\partial \mu}\left[\frac{1}{\sqrt{2\pi}\sigma} \int_{\frac{\ln D_i^{(m)} - \mu}{\sqrt{2}\sigma}}^{\frac{\ln D_{i+1}^{(m)} - \mu}{\sqrt{2}\sigma}} e^{-y^2} dy\right] \\ &= \frac{1}{\sqrt{2\pi}\sigma}\left(exp^{-\frac{\left(\ln D_{i+1}^{(m)} - \mu\right)^2}{2\sigma^2}} - exp^{-\frac{\left(\ln D_i^{(m)} - \mu\right)^2}{2\sigma^2}}\right) \end{aligned} \tag{6}$$

Similarly,

$$\frac{\partial F_i}{\partial \sigma}(\mu,\sigma) = \frac{1}{\sqrt{2\pi}\sigma^2}\left[\left(\ln D_i^{(m)} - \mu\right) exp^{-\frac{\left(\ln D_i^{(m)} - \mu\right)^2}{2\sigma^2}} - \left(\ln D_{i+1}^{(m)} - \mu\right) exp^{-\frac{\left(\ln D_{i+1}^{(m)}\right.}{2\sigma^2}}\right. \tag{7}$$

Moreover, the gradient of objective function $f(\mu,\sigma)$ is

$$\nabla f(\mu,\sigma) = \nabla F(\mu,\sigma)^T F(\mu,\sigma) \tag{8}$$

Table S2 gives the algorithms for solving distribution parameter $\{\mu_m\}_{m=1}^{k}$, $\{\sigma_m\}_{m=1}^{k}$. The results of μ and σ of corresponding powders are shown in Table S3.

Table S2

Algorithm of data processing

Algorithm 1: Solving parameters $\{\mu_m\}_{m=1}^{k}$, $\{\sigma_m\}_{m=1}^{k}$ and $\{p_m\}_{m=1}^{k}$

(a) For a fixed m ($m = 1,2,\cdots,k$), we give the initial point $(\mu^{(0)},\sigma^{(0)})$, a constant $\rho \in (0,1)$, $\delta \in (0,1/2)$ and precision parameter $\epsilon > 0$, let $s = 0$;

(b) If $\|\nabla f(\mu^{(s)},\sigma^{(s)})\|_F \le \epsilon$, then we got $(\mu^{(s)},\sigma^{(s)})$, turn to Step (e);

Else, Solve Levenberg-Marquardt linear equations:

$$\left[\nabla F(\mu^{(s)},\sigma^{(s)})^T \nabla F(\mu^{(s)},\sigma^{(s)}) + \lambda_s I\right] d + \nabla F(\mu^{(s)},\sigma^{(s)})^T \nabla \tag{9}$$

to get the direction $d^{(s)}$ (where $\lambda_s > 0$ is a parameter to promise the coefficient matrix is positive and thus the solution is unique)

(c) Find the step α_s to be the largest number in $\{\rho^i | i = 0,1,2,\cdots\}$ satisfy:

$$f(\mu^{(s+1)},\sigma^{(s+1)}) \le f(\mu^{(s)},\sigma^{(s)}) + \alpha_s \delta \nabla f(\mu^{(s)},\sigma^{(s)})^T d^{(s)} \tag{10}$$

where $(\mu^{(s+1)},\sigma^{(s+1)}) = (\mu^{(s)},\sigma^{(s)}) + \alpha_s d^{(s)}$;

(d) Record $(\mu^{(s+1)},\sigma^{(s+1)})$, let $s = s + 1$ and turn to Step (b);

(e) When $(\mu^{(s)},\sigma^{(s)})$ reach the precision, which means satisfies $\|\nabla f(\mu^{(s)},\sigma^{(s)})\|_F \le \epsilon$,then we get $(\mu^{(s)},\sigma^{(s)})$ as μ_m and σ_m. Substitute μ_m and σ_m into Eq. 1 to get the corresponding p_m. Finally, $\{\mu_m\}_{m=1}^{k}$, $\{\sigma_m\}_{m=1}^{k}$ and

$\{p_m\}_{m=1}^{k}$ of k different kinds of fillers could be obtained by the same method above for different m.

Table S3

Distribution parameters μ and σ of three graphite powders

	G-31	G-13	G-3
μ	3.41	2.45	0.95
σ	0.17	0.51	0.33

Step 2: Mathematical modeling

Suppose we need to mix k powders of different particle sizes distribution, and the filling ratio in the formula is $\{t_m\}_{m=1}^{k}$ ($\sum_{m=1}^{k} t_m = 1$，$t_m \geq 0$). Our goal is to find the best proportion $\{t_m\}_{m=1}^{k}$ so that the mixed proportion approaches the Dinger-Funk equation $U(\cdot)$ [1],

$$U(D_p) = 100\frac{D_p^n - D_{min}^n}{D_{max}^n - D_{min}^n} \tag{11}$$

where $n = 0.37$, D_{min} and D_{max} are the minimum and maximum particle size of the powder. This process can be transformed into mathematical forms:

$$\begin{aligned} \min_{t_m \geq 0, m=1,\cdots,k} \quad & \left\| \int_{D_{min}}^{\cdot} \sum_{m=0}^{k} t_m p_m(x)dx - U(\cdot) \right\|_{L^2([D_{min}, D_{max}])} \\ s.t. \quad & \sum_{m=0}^{k} t_m = 1, t_m \geq 0. \end{aligned} \tag{12}$$

Expand the objective function of Eq. 12, and the above formula is equivalent to:

$$\begin{aligned} \underset{t_m \geq 0, m=1,\cdots,k}{min} \quad & \int_{D_{min}}^{D_{max}} \left| \int_{D_{min}}^{y} \sum_{m=0}^{k} t_m p_m(x) dx - U(y) \right|^2 dy \\ s.t. \quad & \sum_{m=0}^{k} t_m = 1 \\ & t_m \geq 0, m = 1,2,\cdots k. \end{aligned} \tag{13}$$

Eventually, we get the standard form of quadratic programming:

$$\begin{aligned} \underset{t}{min} \quad & \frac{1}{2} t^T H t + f^T t \\ s.t. \quad & \sum_{m=0}^{k} t_m = 1, \\ & t_m \geq 0, m = 1,\cdots,k. \end{aligned} \tag{14}$$

where, $H = (H_{i,j})_{k \times k}$ and $f = (f_1, f_2, \cdots, f_k)^T$ are shown as follow:

$$\begin{aligned} H_{i,j} &= 2 \int_{D_{min}}^{D_{max}} \left[\int_{D_{min}}^{y} p_i(x) dx \cdot \int_{D_{min}}^{y} p_j(x) dx \right] dy, \\ f_i &= -2 \int_{D_{min}}^{D_{max}} \left[\int_{D_{min}}^{y} p_i(x) dx \cdot U(y) \right] dy. \end{aligned} \tag{15}$$

Here, H and f are respectively the constant matrix and constant vector after $\{p_m(\cdot)\}_{m=1}^{k}$, D_{max} and D_{min} are known. The solution $t = (t_1, t_2, \cdots, t_k)^T$ of Eq. 14 is the best proportioning in this algorithm. However, the complete model still requires to calculate the values of *H* and *f*. The solution process of matrix *H* and vector *f* are shown in Table S4. Through the calculation below, the matrix *H* and vector *f* of our powders in Eq. 15 are obtained as follows:

$$H = \begin{pmatrix} 133.50 & 113.68 & 78.50 \\ 113.68 & 106.26 & 77.99 \\ 78.50 & 77.99 & 72.71 \end{pmatrix}, \quad f = \begin{pmatrix} -94.09 \\ -86.52 \\ -66.87 \end{pmatrix}. \tag{16}$$

After obtaining the values of H and f, we completely establish the whole mathematical model.

Table S4

Algorithm for solving H and f.

Algorithm 2: Solving parameters $(H_{i,j})_{k\times k}$ and $\{f_i\}_{i=1}^{k}$

Calculate $(H_{i,j})_{k\times k}$:

(a) Using the compound trapezoidal formula to calculate $H_{i,j}$ as:

$$H_{i,j} = 2t\left[\frac{1}{2}h_{i,j}(D_{min}) + h_{i,j}(x_1) + h_{i,j}(x_2) + \cdots + h_{i,j}\left(x_{n_1-1}\right) + \frac{1}{2}h_{i,j}(D_{m} \tag{17}$$

where $h_{i,j}(x) = \int_{D_{min}}^{x} p_i(x)dx \cdot \int_{D_{min}}^{x} p_j(x)dx$ is the integrand function, $t = (D_{max} - D_{min})/n_1$ is length of each divided interval and n_1 (we set $n_1 = 1000$) is the number of divided intervals in the outer integral $H_{i,j}$,

(b) The value of $h_{i,j}(x_l)$ can similarly be solved by Compound Trapezoidal Formula, where $p_i(x)$ have given by Algorithm 1, $x_l = D_{min} + l \times t$, for $l = 0,1,\cdots,n_1$.

$\{f_i\}_{i=1}^{k}$ can be solved by the same method.

Step 3: Model solving.

By solving quadratic programming problem Eq. 14, the percentage ratio of G-3, G-13, and G-31 as the multi-scale hybrid powder fillers had been obtained, which is 26.42%, 28.16% and 45.42%. Quadratic programming problem can be solved by calling the quadratic programming API (quadprog []) in MATLAB or the cvxpy library function in Python.

The code is available in: https://github.com/dagaishizy/Quadratic-programming-for-optimum-formulation-of-multi-scale-spherical-graphite-particles

References

[1] D. R. Dinger, J. E. Funk, MRS. Bulletin, 1997, 22, 19-23.