

· 研究论文 ·

基于最小热阻路径的聚合物/片状填料复合材料导热模型研究

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摘要 基于有效介质理论的传统导热模型建立在单一颗粒的假设之上,难以刻画填料粒子因距离靠近产生的相互作用及其引起的热流方向变化,因此无法有效表达导热逾渗行为,在高填充条件下预测偏差显著.为此,我们前期提出了基于最小热阻路径理论的导热模型,通过约束热流沿体系中总热阻最小的路径传递,实现了对高填充聚合物/类球形填料复合体系热导率的准确预测.在此基础上,本研究进一步将最小热阻路径的思想拓展至片状填料复合体系.通过将高度无序、空间关联复杂的片状填料分布等效为可解析的简化热阻网络结构,并引入最小热阻路径理论的方向性选择机制,刻画热流的矢量属性,从而能够有效捕捉由片状填料彼此靠近、搭接及网络贯通所引起的逾渗及各向异性导热行为.通过跨材料体系的实验数据验证,该模型在超过200组片状填料复合材料数据上的拟合度达到0.98,平均相对误差仅为11.54%,预测范围覆盖至50 vol%,基本涵盖当前可加工的片状填料复合材料体系.该模型为聚合物/片状填料复合材料体系导热性能的预测提供了一种高效可靠的工具,也为理解聚合物复合材料的导热逾渗行为提供了一定的理论依据.

关键词 片状填料; 聚合物复合材料; 理论模型; 导热系数; 导热逾渗

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高导热且具备定向热传输能力的聚合物复合材料在电子封装、柔性电子器件以及高功率密度热管理等领域展现出广阔的应用前景^[1–5]. 聚合物本征导热能力有限,其复合体系的整体导热性能在很大程度上依赖于高导热填料的引入以及填料在基体中的空间分布特征^[6–9]. 具有高长径比和显著各向异性的二维片状填料(如氮化硼、石墨、石墨烯等)因其优异的面内热导率和易取向特性,被广泛用于构建定向导热通路,从而在较低填充条件下实现高效的导热增强^[10–14]. 尽管实验研究在揭示聚合物复合材料导热性能方面取得了大量进展,但传统实验手段难以对组分参数与微观结

构对导热行为的贡献进行定量区分;对于未知体系,其配方优化与结构设计仍高度依赖反复试验与性能测试,成本高、效率低,从而在一定程度上制约了对导热增强机理的深入理解^[15–18]. 因此,发展能够预测聚合物/片状填料复合材料导热性能并揭示其导热机制的理论模型,对于高导热聚合物复合材料的合理设计与机理分析都具有重要的指导意义.

基于经典有效介质理论的导热模型通常将复合体系视为宏观均匀连续介质,通过场量平均的方法预测有效热导率.例如,Maxwell-Garnett模型^[19–21]利用拉普拉斯方程描述了单一颗粒嵌入连

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续基体中的稳态温度场分布,建立了复合材料有效热导率与各组分热导率及体积分数的解析关系,奠定了有效介质导热模型的基础.在此基础上,Hamilton等^[22]通过引入形状因子扩展了有效介质理论在片状填料体系中的适用性;Hasselman和Johnson^[23]进一步在稳态热场边界条件中显示引入界面热阻与取向因子,提高了模型在低填充分数条件下的预测精度.随后,Hatta等^[24]和Nan等^[25]通过引入片状填料的长径比等结构参数,使其能够在一定程度上描述复合体系中片状填料结构的各向异性特征.然而,上述模型本质上仍建立在均匀分散和弱填料相互作用的假设之上.对于高长径比的片状填料而言,其较大的比表面积使其在较低填充分数下即可形成贯通的二维导热网络,此时热流不再均匀分布,而是倾向于沿由填料取向、搭接方式及界面性质共同决定的最小总热阻路径选择性传输,从而表现出显著的方向依赖性和非均匀热传导行为.基于单一颗粒和均匀分散假设的经典有效介质导热模型难以描述此类导热网络的形成与演化过程,也难以刻画热流的方向选择性传输行为.

在前期研究中,本课题组^[26]针对类球形填料体系提出了一种基于最小热阻路径的导热模型.该模型通过约束热流优先沿体系中总热阻最小的路径传递,在定量计算热传输阻力的同时,引入了热流的方向选择机制,从而有效捕捉了高填充条件下粒子间距缩小和填料相互作用增强对导热性能的关键影响,实现了对高填充体系热导率的准确预测.在此基础上,本研究进一步将最小热阻路径的思想拓展至片状填料复合体系,利用最小热阻路径理论的方向性选择机制,准确刻

画热流的矢量属性,使其在多通路体系中优先沿最小热阻方向传输,从而有效捕捉片状填料体系中由填料取向、彼此靠近、搭接与网络贯通所引起的各向异性导热行为.此外,通过提出“取向平均场”和“等效准对齐构型”的假设,将高度无序、空间关联复杂的片状填料分布等效为可解析的简化热阻网络结构,并在模型构建过程中,系统引入填料长径比、取向因子、填料-基体界面热阻及填料-填料接触热阻等关键参数,实现了对微观结构、导热通路连通性、界面效应的定量描述.利用跨体系实验数据对模型的准确性和适用范围进行验证,结果表明:所提出的片状填料导热模型(platelet-based model)对超过200组数据拟合度高达0.98,平均相对误差仅为11.54%,预测范围覆盖至50%,基本覆盖当前可加工的异型填料复合材料体系.本研究所构建的模型为未知体系的有效热导率的预测提供了便捷而可靠的方法和工具,且能够定量分析填料尺寸、界面热阻、接触热阻等因素对导热率及其增长趋势的影响,对理解片状填料填充复合材料中的导热逾渗现象具有重要的指导意义.由于其良好的可扩展性,该建模框架亦可推广应用于其他形貌或多组分填料体系,有望为构建更具普适性的导热预测理论提供新的思路和可能.

1 模型构建方法

1.1 模型结构简化方法

图1展示了片状填料体系中复杂填料分布的简化过程以及最小热阻传输路径的形成机制.真实复合体系中的片状填料分布高度无序,难以用简单的数学参数来描述复杂的结构特征,因此本

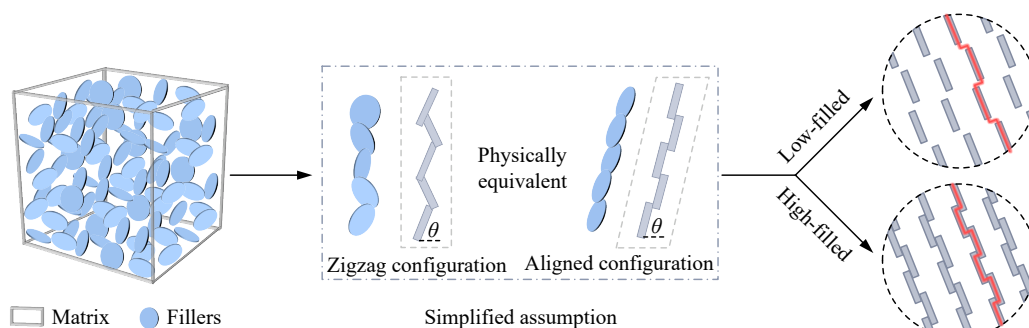


Fig. 1 Schematic illustration of the structural simplification for platelet-based composites, in which a highly disordered realistic microstructure is reduced to an equivalent uniformly oriented configuration. The composite is further classified into low-filled and high-filled regimes according to the formation of continuous thermal conduction pathways, where the red lines indicate the least-resistance pathway.

研究在模型构建时引入3个基本假设. 首先, 由于填料网络的形成会促进热流沿其构建的连续通路传递^[27~29], 提出假设①: 2个相邻填料之间的热流主要沿其相互连接所构建的最小热阻路径传输; 其余聚合物基体部分与该路径以并联形式共同参与热传递. 其次, 宏观复合材料中片状填料在热流方向上的取向角度各异, 直接描述其取向统计特征通常十分困难, 而填料整体取向状态的平均取向度容易由实验表征, 用以表征填料在体系中的宏观分布特征. 因此提出假设②: 体系中所有填料具有一致的取向角度 θ , 即其所有填料的取向方向与其宏观面内取向度 f 相同, 满足关系式 $f = \frac{3\cos^2\theta - 1}{2}$. 在此约束条件下, 片状填料

仍可在热流垂直方向上发生局部旋转, 使得最小热阻路径在微观尺度上呈现锯齿状, 从而增加模型求解的复杂性. 而根据傅里叶定律 $R = \frac{d}{A_{//}k}$ 可知热流传递效率主要由片状填料在热流方向上的有效投影面积 $A_{//}$ 决定, 其局部旋转仅改变热通路的几何连接形态, 而对传热方向的等效热阻影响有限^[30]. 基于上述分析, 进一步提出假设③: 所有填料的取向角度完全一致, 从而将复杂的锯齿状通路转变为在热传输上等效的准对齐构型. 此简化在物理机理和数学描述上均保持一致性, 可在不削弱关键传热机制的前提下显著降低模型复杂度. 另外, 高长径比的填料体系通常会在较低的体积分数下形成连续的导热网络结构, 该临界体积分数通常与填料的长径比相关^[31,32]. 因此在该模型构建过程中, 规定 $V_{f0} = \frac{d}{2a}$ 为临界体积分数, 其中 d 为片状填料的厚度, a 为填料的半径. 当体积分数低于该临界值时, 填料粒子独立分布, 热流传递的最小阻力路径中需经过一段聚合物基体, 我们将其归类为低填充体系; 当体积分数高于该临界值时, 最小热阻路径为填料粒子相互搭接形成连续的填料导热网络, 将其归类为高填充体系.

1.2 基于最小热阻理论的模型推导框架

简化的导热网络可以划分为多个具有相同取向角度的结构单元构成的重复单元体系. 在每个结构单元中, 片状填料的面内热导率($k_{f//}$)和面外热导率($k_{f\perp}$)存在差异, 因此结构单元的面外导热($k_{\perp}$)和面内导热($k_{//}$)对整体热传导的贡献不同. 其

相对贡献由填料的取向度决定, 因此复合材料的有效面内与面外热导率可以表示为由取向度加权的 $k_{\perp}$ 与 $k_{//}$ 的组合关系:

$$k_{eff\perp} = k_{\perp}\cos^2\theta + k_{//}\sin^2\theta \quad (1)$$

$$k_{eff//} = k_{//}\cos^2\theta + k_{\perp}\sin^2\theta \quad (2)$$

基于此, 复合材料有效热导率可以通过计算结构单元的面内及面外等效热导率, 并结合取向参数 $\cos^2\theta$ 进行求解. 进一步地, $k_{\perp}$ 和 $k_{//}$ 均可表示为填料热导率 k_f 、聚合物热导率 k_m 、填料半径 r 、填料厚度 d 、体积分数 V_f 、填料与基体的界面热阻 R_i 、填料之间的接触热阻 R_c 的函数, 因此复合材料有效热导率可表示为:

$$k_{eff} = f(k_f, k_m, a, d, V_f, R_i, R_c, \theta \dots) \quad (3)$$

针对低填充和高填充体系面内和面外方向的有效热导率的计算, 由于最小热阻路径的组成存在差异, 所以2类体系的计算方式不同. 图2和图3进一步给出了结构单元在面内与面外方向用于计算热导率的几何划分方式及相关参数分布. 结构单元的几何尺寸 X 、 Y 、 Z 可以通过联立填料尺寸及复合材料体积分数求解, 而结构单元中各部分热阻可依据傅里叶定律进行计算. 下文将按照低填充和高填充2种情形分别给出公式推导过程.

1.2.1 低填充片状填料体系的模型推导

低填充分数下, 结构单元的几何参数分别为 X_1 、 Y_1 、 Z_1 , 其中 X_1 决定了相邻2个片状填料的距离, 如图2所示. 当 $V_f=0$ 时, 结构单元为纯聚合物基体, 需要包含一颗填料粒子的几何结构需要 X_1 为无穷大; 当 $V_f = \frac{d}{2a}$ 时, 几何参数 $X_1=2a$, 此时两个相邻的片状填料正好接触, 结构单元的长度为一个填料的直径. 根据在临界体积分数附近填料恰好发生搭接的构型设定, X_1 可以设置为与体积分数相关参数, 从而保证结构单元几何尺寸与填料网络的演化保持一致:

$$X_1 = \frac{d + 2aV_f}{2V_f} \quad (4)$$

由此定义的 X_1 关于 V_f 的函数可直接量化相邻填料粒子的平均距离随体积分数增加而单调减小的关系. 进一步假设结构单元在非传热方向上的特征尺度与填料自身的几何比例保持一致, 即 Y_1 和 Z_1 与填料的半径和厚度成正比, 确保单元结构在各个方向的尺寸都随着 V_f 协调变化, 因此有:

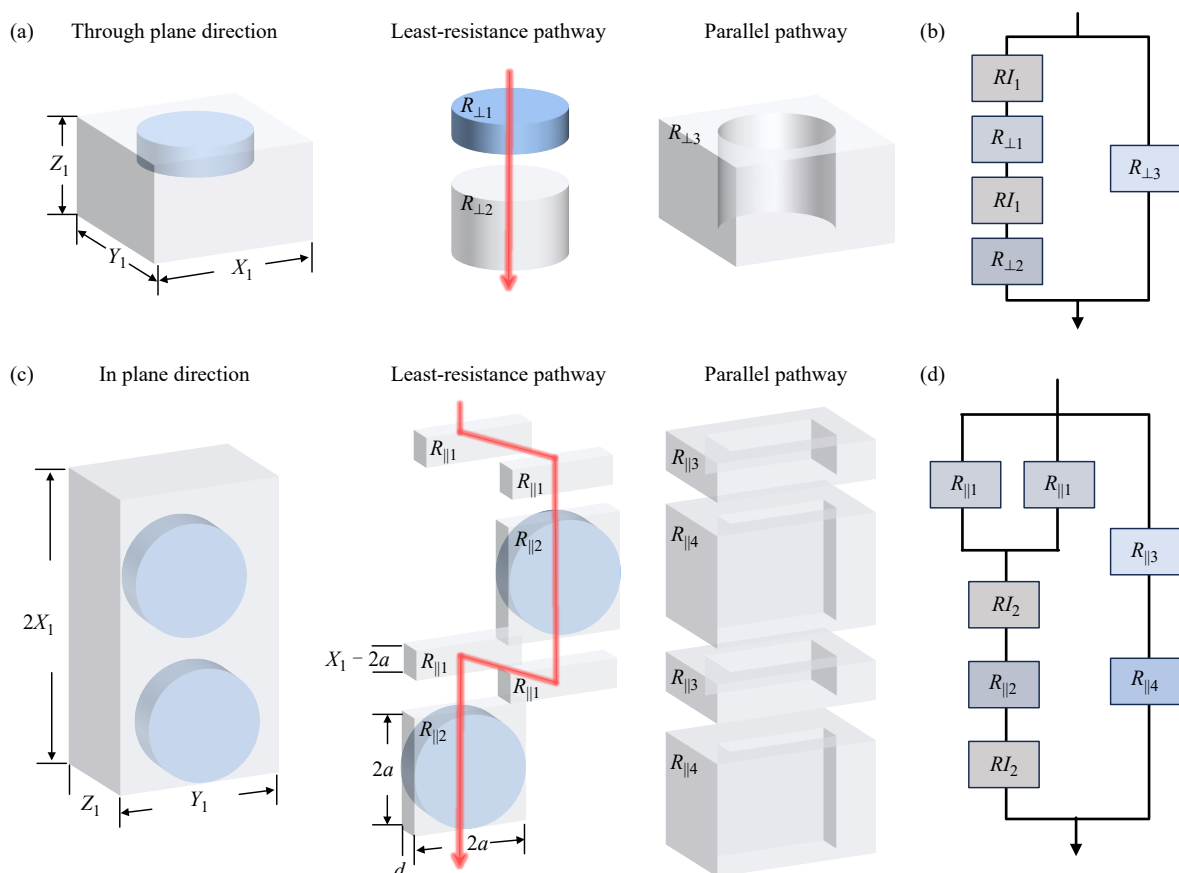


Fig. 2 Schematic of the thermal resistance network in low-filled composites. (a) Decomposition of the structural unit and the corresponding thermal resistance components for in-plane thermal conductivity; (b) Thermal resistance configuration in the in-plane direction; (c) Decomposition of the structural unit and the corresponding thermal resistance components for through-plane thermal conductivity; (d) Thermal resistance configuration in the through-plane direction.

$$\frac{Y_1}{Z_1} = \frac{a}{d} \quad (5)$$

同时, 结构单元的体积分数满足:

$$V_f = \frac{\pi a^2 d}{X_1 Y_1 Z_1} \quad (6)$$

联立式(4)~(6), 可求解得到 Y_1 、 Z_1 分别为:

$$Y_1 = \sqrt{\frac{2\pi a}{2aV_f + d}} a \quad (7)$$

$$Z_1 = \sqrt{\frac{2\pi a}{2aV_f + d}} d \quad (8)$$

基于以上参数对结构单元热导率求解.

面外方向有效热导率求解. 如图2(a)和2(b)所示, 规定片状填料投影所在圆柱部分为面外方向(垂直填料平面)的最小热阻路径, 由填料贡献的热阻 $R_{\perp 1}$ 、聚合物基体贡献的热阻 $R_{\perp 2}$ 及填料与聚合物间的界面热阻 RI_1 串联构成, 剩余聚合物区域 $R_{\perp 3}$ 与之并联, 共同决定结构单元的面外热导率. 推导过程如下:

$$R_{\perp 1} = \frac{d}{\pi a^2 k_{f\perp}} \quad (9)$$

$$RI_1 = \frac{R_i}{\pi a^2} \quad (10)$$

$$R_{\perp 2} = \frac{Z_1 - d}{\pi a^2 k_m} \quad (11)$$

$$R_{\perp 3} = \frac{Z_1}{(X_1 Y_1 - \pi a^2) k_m} \quad (12)$$

$$R_{\perp \text{least}} = R_{\perp 1} + R_{\perp 2} + 2RI_1 \quad (13)$$

$$R_{\perp} = \frac{1}{\frac{ij}{hR_{\perp \text{least}}} + \frac{ij}{hR_{\perp 3}}} \quad (14)$$

面外热导率可表示为:

$$k_{\perp} = \frac{\sum_0^h Z_1}{\left(\sum_0^i X_1\right) \cdot \left(\sum_0^j Y_1\right) \cdot R_{\perp}} \quad (15)$$

其中 i , j , h 分别表示复合材料在宏观尺度 X , Y , Z 方向上包含的结构单元个数.

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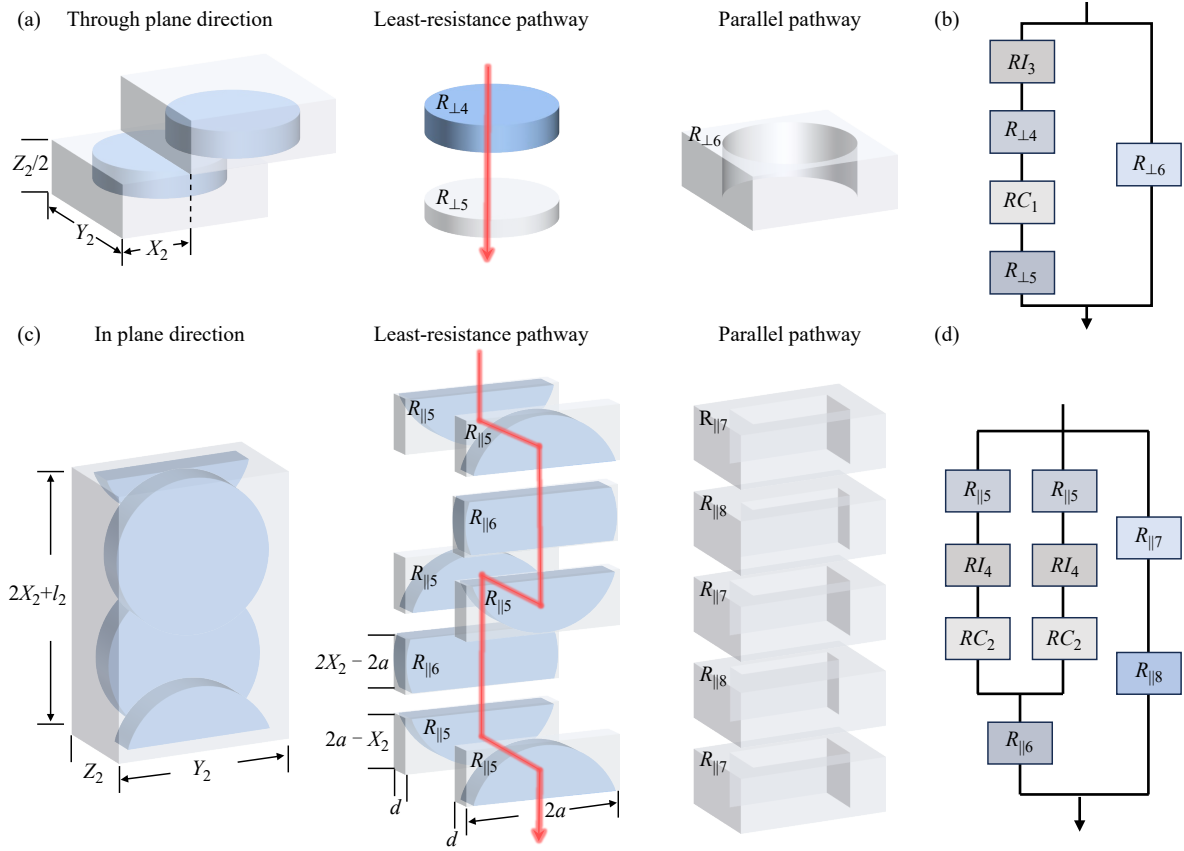


Fig. 3 Schematic of the thermal resistance network in high-filled composites. (a) Decomposition of the structural unit and the corresponding thermal resistance components for in-plane thermal conductivity; (b) Thermal resistance configuration in the in-plane direction; (c) Decomposition of the structural unit and the corresponding thermal resistance components for through-plane thermal conductivity; (d) Thermal resistance configuration in the through-plane direction.

$$k_{\perp} = k_m + \frac{\pi a^2 k_m (d(k_m - k_{f\perp}) + 2k_{f\perp} k_m R_i)}{X_1 Y_1 (d(k_{f\perp} - k_m) - k_{f\perp} (2k_m R_i + Z_1))} \quad (16)$$

面内方向有效热导率求解. 如图 2(c) 和 2(d) 所示, 面内方向(平行填料平面)的最小热阻路径将 2 个片状填料相连, 由并联的聚合物部分 $R_{\parallel 1}$ 、聚合物和填料共混物 $R_{\parallel 2}$ 和聚合物与填料的界面热阻 RI_2 串联形成, 剩余的聚合物 $R_{\parallel 3}$ 和 $R_{\parallel 4}$ 串联为平行路径与最小热阻路径并联. 其中, 最小热阻路径中各部分热阻的传热面积均为片状填料在传热方向的投影面积. 具体推导过程如下:

$$R_{\parallel 1} = \frac{X_1 - 2a}{2adk_m} \quad (17)$$

$$R_{\parallel 2} = \frac{2a}{2ad \left(\frac{\pi}{4} k_{f\parallel} + \frac{4-\pi}{4} k_m \right)} \quad (18)$$

$$k_{\parallel} = \frac{k_m X_1}{Y_1 Z_1} \left(\frac{4\pi ad (\pi k_{f\parallel} + (4-\pi) k_m)}{16\pi a k_m + (8k_m R_i + \pi(X_1 - 2a))(\pi k_{f\parallel} + (4-\pi) k_m)} + \frac{1}{\frac{X_1 - 2a}{Y_1 Z_1 - 4ad} + \frac{2a}{Y_1 Z_1 - 2ad}} \right) \quad (26)$$

$$RI_2 = \frac{R_i}{\pi ad} \quad (19)$$

$$R_{\parallel \text{least}} = \frac{1}{\frac{1}{R_{\parallel 1}} + \frac{1}{R_{\parallel 2}}} + R_{\parallel 3} + 2RI_2 \quad (20)$$

$$R_{\parallel 3} = \frac{X_1 - 2a}{(Y_1 Z_1 - 4ad)k_m} \quad (21)$$

$$R_{\parallel 4} = \frac{2a}{(Y_1 Z_1 - 2ad)k_m} \quad (22)$$

$$R_{\parallel p1} = R_{\parallel 3} + R_{\parallel 4} \quad (23)$$

$$R_{\parallel} = \frac{1}{\frac{hj}{iR_{\parallel \text{least}}} + \frac{hj}{iR_{\parallel p1}}} \quad (24)$$

最终, 面内热导率可表示为:

$$k_{\parallel} = \frac{\sum_0^i X_1}{\left(\sum_0^h Z_1 \right) \cdot \left(\sum_0^j Y_1 \right) \cdot R_{\parallel}} \quad (25)$$

化简得到面内热导率的表达式如下:

1.2.2 高填充片状填料体系的模型推导

在高填充分数下, 当 $V_f = \frac{d}{2a}$ 时, 两个相邻的片状填料恰好发生接触, 此时结构单元的几何参数为 $X_2 = 2a$; 当 $V_f = \frac{\pi}{4}$ 时, 对应于该模型的理论预测最高体积分数, 在错位排布结构中, 同一层的片状填料也发生接触, 此时 $X_2 = a$. 同样, Y_2 和 Z_2 按填料几何尺寸比例分配. 因此结构单元的几何参数分别为 X_2 、 Y_2 、 Z_2 , 可以列出等式:

$$X_2 = \frac{2(\pi a^2 - ad - 2a^2 V_f)}{\pi a - 2d} \quad (27)$$

$$\frac{Y_2}{Z_2} = \frac{a}{d} \quad (28)$$

$$V_f = \frac{\pi a^2 d}{X_2 Y_2 Z_2} \quad (29)$$

联立式(27)~(29), 可以得到 Y_2 、 Z_2 分别为:

$$Y_2 = a \sqrt{\frac{\pi(\pi a - 2d)}{2V_f(\pi a - 2aV_f - d)}} \quad (30)$$

$$Z_2 = d \sqrt{\frac{\pi(\pi a - 2d)}{2V_f(\pi a - 2aV_f - d)}} \quad (31)$$

面外方向有效热导率求解. 如图 3(a) 和 3(b) 所示, 面外方向的最小热阻路径由填料贡献的热阻 $R_{\perp 4}$ 、聚合物基体贡献的热阻 $R_{\perp 5}$ 、填料与聚合物间的界面热阻 RI_3 及填料与填料的界面热阻 RC_1 串联构成, 剩余聚合物区域 $R_{\perp 6}$ 与之并联,

$$k_{\perp} = \left(1 - \frac{\pi a^2}{2X_2 Y_2}\right) k_m + \frac{\pi a^2 Z_2}{4XY \left(\frac{100R_c(\pi a - 2d)}{2aV_f - d} + \frac{100R_i(\pi a - 2d)}{100\pi a - 2aV_f - 199d} + \frac{d}{k_{f\perp}} + \frac{Z_2 - 2d}{2k_m} + R_i \right)} \quad (40)$$

面内方向有效热导率求解. 如图 3(c) 和 (d) 所示, 面内方向(平行填料平面)的最小热阻路径完全由聚合物和填料的共混物组成, 其中 2 个 $R_{\parallel 5}$ 并联, 且同时包含界面热阻 RI_4 与接触热阻 RC_2 ; 该并联结构与 $R_{\parallel 6}$ 串联, 共同构成最小热阻路径的总热阻; 剩余的聚合物 $R_{\parallel 7}$ 和 $R_{\parallel 8}$ 串联为平行路径与最小热阻路径并联. 推导过程如下:

$$R_{\parallel 5} = \frac{2a - X_2}{2ad \left(\frac{\pi}{4} k_{\parallel} + \frac{4 - \pi}{4} k_m \right)} \quad (41)$$

$$R_{\parallel 6} = \frac{2X_2 - 2a}{2ad \left(\frac{\pi}{4} k_{\parallel} + \frac{4 - \pi}{4} k_m \right)} \quad (42)$$

$$RI_4 = \frac{R_i}{\pi ad} \quad (43)$$

有效热导率推导过程如下:

$$R_{\perp 4} = \frac{d}{\pi a^2 k_{f\perp}} \quad (32)$$

$$R_{\perp 5} = \frac{\frac{Z_2}{2} - d}{\pi a^2 k_m} \quad (33)$$

由于真实构型中片状填料具有空间旋转, 其相互接触难以形成大面积贴合, 填料主要呈现多点式接触^[33-35]. 因此, 引入接触热阻 R_c 时, 假设当填充分数达到模型上限 $V_{fmax} = \frac{\pi a^2 d}{4a^2 d} \approx 78\%$ 时, 填料间有效接触面积为其总表面积的 1/100.

$$RC_1 = \frac{R_c}{\frac{\pi a^2}{100} \cdot \frac{2aV_f - d}{\pi a - 2d}} \quad (34)$$

$$RI_3 = \frac{R_i}{\pi a^2} + \frac{R_i}{\pi a^2 \left(1 - \frac{1}{100} \cdot \frac{2aV_f - d}{\pi a - 2d} \right)} \quad (35)$$

$$R_{\perp 6} = \frac{\frac{Z_2}{2}}{2X_2 Y_2 k_m} \quad (36)$$

$$R_{\perp least2} = R_{\perp 4} + R_{\perp 5} + RI_3 + RC_1 \quad (37)$$

$$R_{\perp} = \frac{1}{\frac{ij}{hR_{\perp least2}} + \frac{ij}{hR_{\perp 6}}} \quad (38)$$

$$k_{\perp} = \frac{\sum_0^h \frac{Z_2}{2}}{\left(\sum_0^i 2X_2 \right) \cdot \left(\sum_0^j Y_2 \right) \cdot R_{\perp}} \quad (39)$$

最终, 面外热导率可表示为:

$$RC_2 = \frac{R_c}{\frac{\pi a^2}{100} \cdot \frac{2aV_f - d}{2(\pi a - 2d)}} \quad (44)$$

$$R_{\parallel least2} = \frac{1}{\frac{1}{R_{\parallel 5} + RI_4 + RC_2} + \frac{1}{R_{\parallel 5} + RI_4 + RC_2}} + R_{\parallel 6} \quad (45)$$

$$R_{\parallel 7} = \frac{2a - X_2}{(Y_2 Z_2 - 4ad) k_m} \quad (46)$$

$$R_{\parallel 8} = \frac{2X_2 - 2a}{(Y_2 Z_2 - 2ad) k_m} \quad (47)$$

$$R_{\parallel p2} = R_{\parallel 7} + R_{\parallel 8} \quad (48)$$

$$R_{\parallel} = \frac{1}{\frac{hj}{iR_{\parallel least2}} + \frac{hj}{iR_{\parallel p2}}} \quad (49)$$

$$k_{\parallel} = \frac{\sum_0^i X_2}{\left(\sum_0^h Z_2\right) \cdot \left(\sum_0^j Y_2\right) \cdot R_{\parallel}} \quad (50)$$

化简得到面内热导率:

$$k_{\parallel} = \frac{X_2}{Y_2 Z_2} \left(\frac{4\pi a^2 d (2aV_f - d) (\pi k_{f\parallel} + (4 - \pi) k_m)}{(4a^2 V_f R_i - 200d^2 R_c + ad(100\pi R_c - 2R_i)) (\pi k_{f\parallel} + (4 - \pi) k_m) + 4\pi a (2aV_f - d) (3X_2 - 2a)} + \frac{2k_m (Y_2 Z_2 - 2ad) (Y_2 Z_2 - 4ad)}{X_2 Y_2 Z_2 - 2ad (3X_2 - 2a)} \right) \quad (51)$$

将以上模型命名为片状填料导热模型(Platelet-based model), 其求解流程可概括为图4所示的计算流程图, 并可通过简洁的程序化实现对模型方程进行高效求解^[36]. 其中 k_f 、 k_m 、 r 、 d 都可以根据所选材料直接通过查阅文献或工具书确定, 而不同体系的 R_i 和 R_c 通常有一定的差异. 一方面可以通过实验方式直接进行测试, 如 3ω 技术、激光闪烁技术、时域热反射技术等方法^[37-41]; 另一方面, 也可以用两组实验数据利用模型直接计算获得, 从而来预测该体系其他体积分数下的有

效热导率. 对于反向求解的实验数据优选网络形成前后各一组数据. 首先利用低填充的数据拟合获得 R_i 的统计平均值, 随后在固定 R_i 的基础上, 结合高填充分数下的导热数据反演 R_c , 从而分别表征 R_i 与 R_c 在不同填充阶段对热导率的主导作用. 若无低填充数据, 2 组高填充数据也可通过求解二元一次方程进行 R_i 和 R_c 的统计平均值求解, 但此时 R_i 和 R_c 会存在一定的参数耦合, 其结果可满足模型预测的数值需求, 但难以准确反映体系内的界面传热性质.

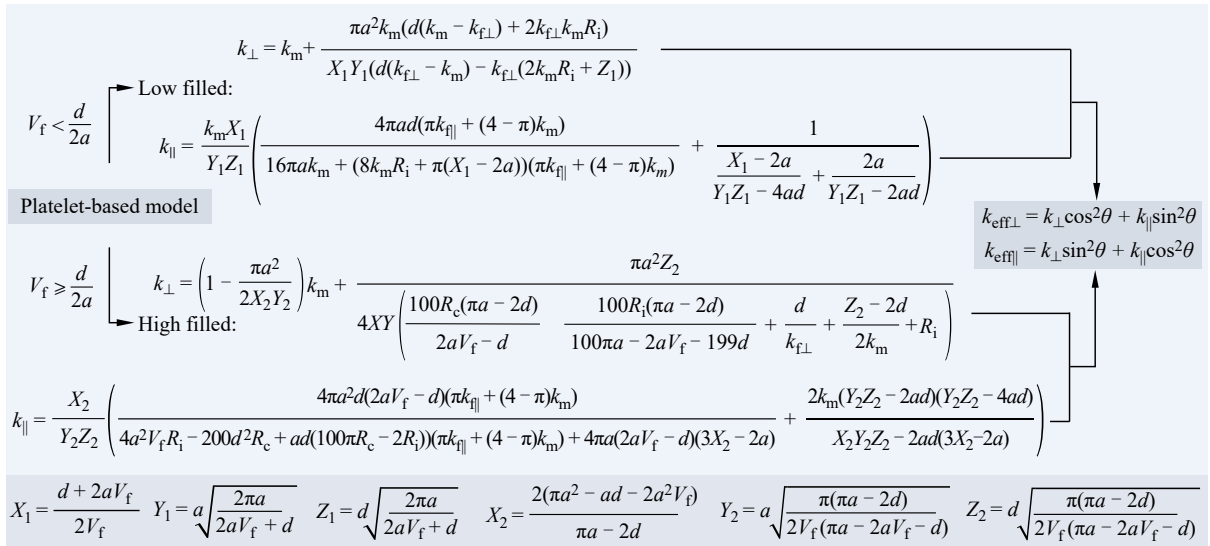


Fig. 4 Schematic of the computational workflow of Platelet-based thermal conductivity model.

2 模型预测准确性与适用性验证

为了验证模型的预测效果, 通过3个指标评测模型预测的有效热导率与材料实际测试的热导率, 以说明模型的预测精度及可靠性.

(1) 预测值与真实值的拟合度:

$$R^2 = 1 - \frac{\sum_{i=1}^n (k_{a,i} - k_{eff,i})^2}{\sum_{i=1}^n (k_{a,i} - \bar{k}_a)^2} \quad (52)$$

拟合度越接近1, 预测相对误差越低, 代表预测值与真实值越接近.

(2) 预测误差:

$$\text{Error} = \frac{k_{eff} - k_a}{k_a} \quad (53)$$

预测误差随机分散, 则代表模型没有明显的高估或低估复合材料的热导率.

(3) 预测平均相对误差:

$$\text{MRE} = \frac{1}{n} \sum_{i=1}^n \frac{|k_{eff,i} - k_{a,i}|}{k_{a,i}} \quad (54)$$

预测平均相对误差越小, 代表模型预测精度越高.

2.1 片状填料导热模型的预测精度及范围验证

本研究共选取了236组片状填料复合材料的实验数据^[36,42-74], 涵盖不同的聚合物类型(环氧树脂、硅橡胶、聚四氟乙烯等)、片状填料种类(氮化硼、石墨烯、氧化石墨烯等)、实际测试热导率(0.2~20 W/(m·K))、测试方法等. 将模型预测的以及实际测试的热导率进行拟合分析, 结果显示传统导热模型 H-J model (-0.27)、Hatta model (-0.29)和 Hamilton model (-0.06)的拟合度(R^2)均小于0 (图5), 难以准确捕捉片状填料在复合材料中形成贯通导热网络所带来的显著热增强效应, 导致预测结果系统性低估材料的实际热导率. 而 Platelet-based model 预测的有效热导率与实际测试的热导率的拟合度高达0.98 (图6(a)), 展现出极高的预测一致性与可靠性. 图6(b)进一步展示了 Platelet-based model 在不同体积分数条件下的预测误差分布, 可见误差均呈现围绕0值随机分布的特征, 表明模型不存在明显系统性偏差, 预测稳定性良好. 模型的预测误差可能来源于输入结构参数本身的测试不确定性, 也可能源于材料热导率测量误差. 此外, 模型建立所依赖的理想化假设与实际填料的空间分布仍不可避免地存在偏差. 尽管如此, 与经典导热模型相比, 其最大预测误差显著降低(<50%), 表明本模型在不同填充分数下表现出更优的预测稳定性与鲁棒性(图6(c)). 从平均相对误差来看, Platelet-based model 的平均预测误差仅为11.54% (图6(d)), 明显优于传统导热模型 H-J model (59.42%)、Hatta model (63.34%)和 Hamilton model (46.28%). 这一优势源于本模型突破了经典有效介质理论基于单一颗粒和均匀分散假设的限制, 通过将复合材料等效为由连续的热阻网络结构并约束热流沿总热阻最小的路径传输, 能够显式刻画片状填料在填充分数提高过程中由彼此靠近、搭接到网络贯通引起的热阻路径重构与方向选择性. 进一步按不同体积分数对验证数据集进行拟合度和误差分析, 结果显示在<10%, 10%~30%, >30%的各个体积分数阶段均具有超过0.95的拟合度和小于15%的预测误差, 展现出全范围内的适用一致性.

2.2 导热逾渗与近线性增强行为的模型化描述

研究发现 Platelet-based model 不仅能准确预测呈现逾渗行为或近线性热导率增长特征的复合体系, 对于具有显著取向效应的各向异性的超高

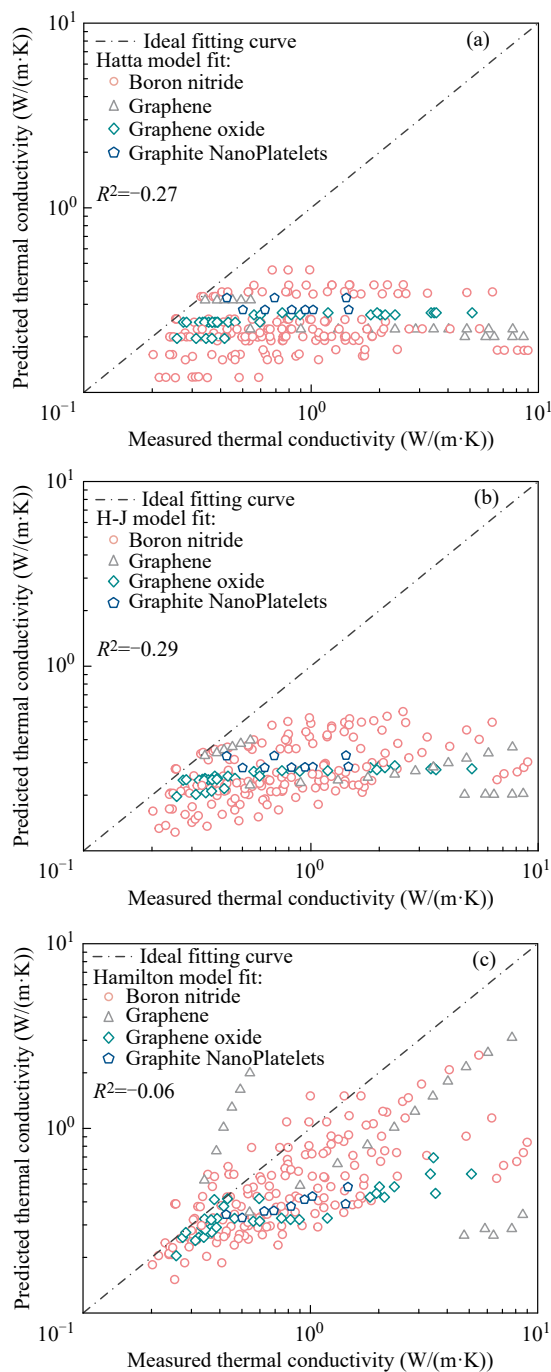


Fig. 5 Fitting analysis of the effective thermal conductivity predicted by classical models versus experimental measurements: (a) Hatta model, (b) Hasselman-Johnson (H-J) model, and (c) Hamilton model.

导热片状填料体系也同样表现出优异的预测精度(如图7所示). 不同于传统渗流理论对逾渗阈值和临界指数的经验拟合, 本模型通过引入填料长径比、界面热阻、接触热阻以及取向度等关键参数, 将导热逾渗刻画为填料几何连通性与界面传输效率协同调控的连续演化过程, 将热导率的突

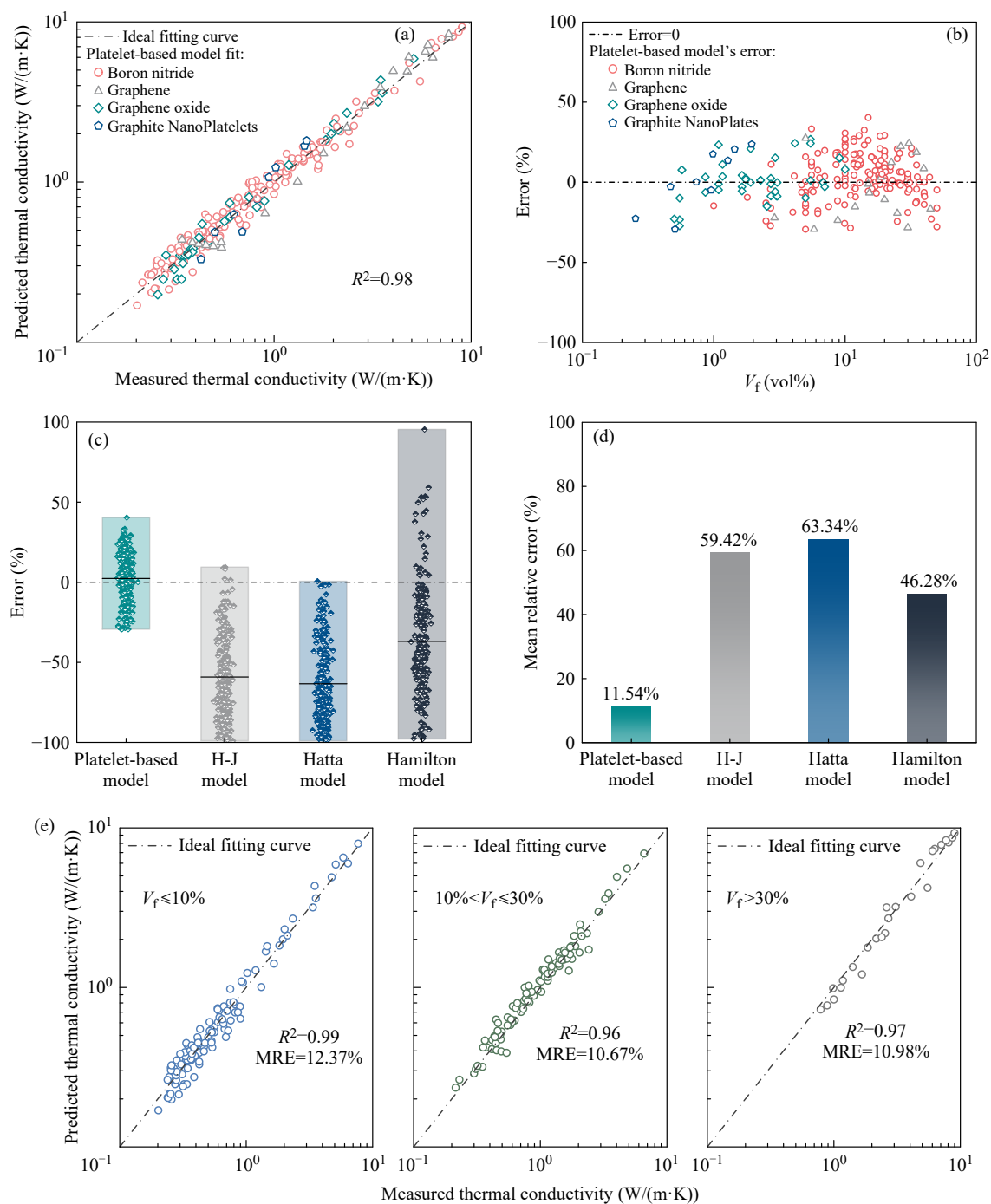


Fig. 6 Fitting performance of the Platelet-based thermal conductivity model. (a) Fitting analysis between predicted and measured values; (b) Error distribution at different filler volume fractions; (c) Comparison of error distributions among different thermal conductivity models; (d) Comparison of mean relative errors of different thermal conductivity models; (e) Fitting performance and mean relative errors across different volume fraction ranges.

变行为直观映射为最小热阻路径等效热阻值的跃迁, 从而赋予模型更清晰的物理图像和预测能力. 如图 7(a) 和 7(b) 的 2 种复合材料均为氮化硼-环氧树脂^[58,74], 但其填料长径比分别为约 100 和 20. 高长径比更容易形成贯通的二维导热网络, 从而表现出逾渗式热导率跃升; 而低长径比的体

系则展现出近线性增长趋势. 此外, 图 7(c) 中呈现的石墨烯-环氧树脂体系在体积分数仅 3% 的填充下, 实现了高达 20 W/(m·K) 的导热, 这既源于石墨烯极高的长径比(约 500), 也得益于其显著的取向行为^[70]. 图 7(d) 给出了该体系的面内热导率预测结果, 通过带入不同的取向度参数,

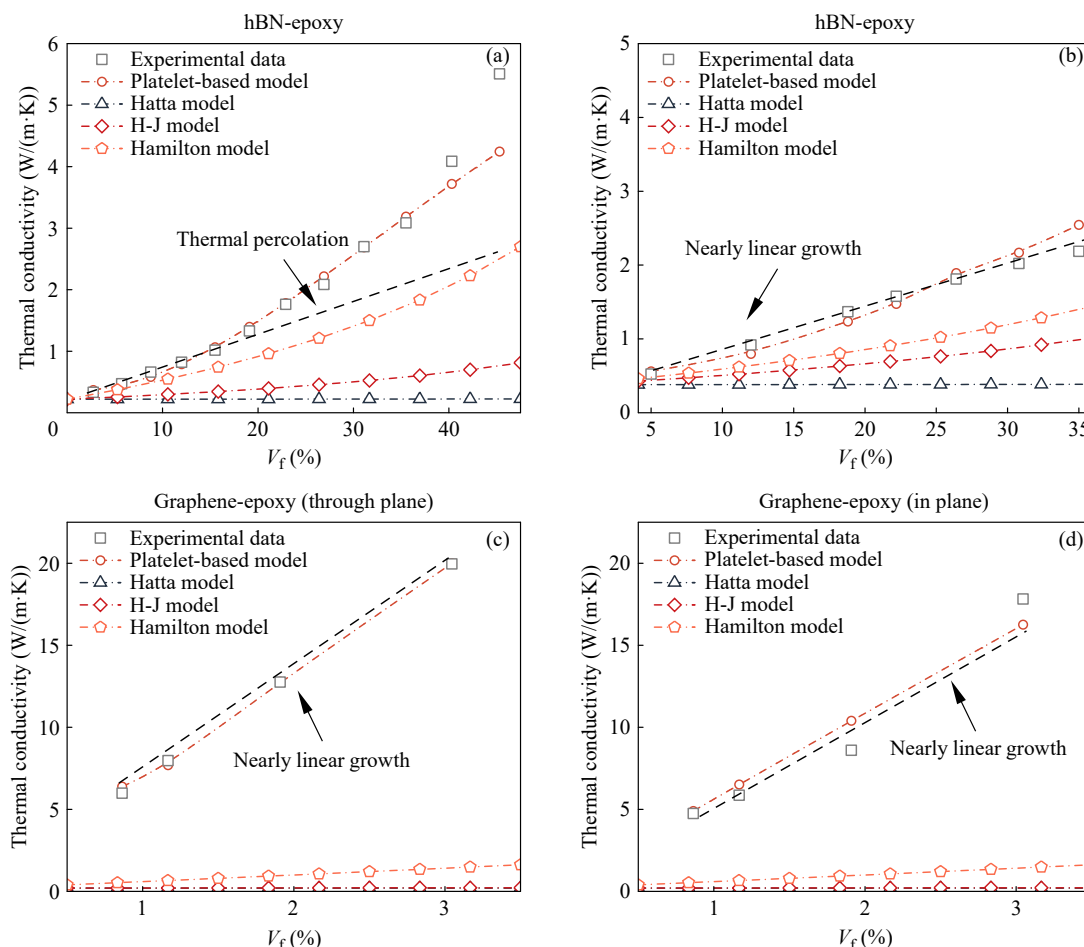


Fig. 7 Fitting performance of Platelet-based model and classic thermal conductivity models (Hatta, H-J, and Hamilton models) for different experimental systems: (a, b) hBN-epoxy, (c) graphene-epoxy (through plane) and (d) graphene-epoxy (in plane).

模型能够有效描述各向异性复合材料热导率随取向演化的变化规律. 此外, 利用两组实验数据拟合得到的 R_i 和 R_c 反映了复合材料中界面热阻和接触热阻的统计平均值, 能够有效反映片状填料体系中不同界面的传热能力. 因此, 为更深入揭示模型的适用范围及关键影响机制, 有必要对这些参数对模型输出的影响进行系统性分析.

图 8(a)~8(d) 展示了不同界面热阻、接触热阻、长径比以及取向度的条件下, 片状填料复合材料的有效热导率随填充体积分数的变化规律. 已有文献报道, 填料-聚合物的界面热阻和填料-填料的接触热阻均分布在 $10^{-9} \sim 10^{-5} \text{ m}^2 \cdot \text{K/W}$ [75~77]. 图 8(a) 和 8(b) 中在控制 $\cos^2\theta=1/3$, 长径比为 100 的前提下, 分别恒定控制 R_i 或 R_c , 然后在理论热阻范围内改变 R_c 或 R_i 的值, 以考察其影响机制. 在图 8(a) 中, 当固定界面热阻 $R_i=10^{-7} \text{ m}^2 \cdot \text{K/W}$ 时, 随着接触热阻 R_c 的降低, 热导率曲线由近线性增长逐渐转变为明显的逾渗特征, 且逾渗起

始体积分数向更低的 V_f 区间移动. 这表明填料与填料界面散射越小, 连通导热网络的逾渗行为越明显. 从最小热阻路径的角度理解, 当 R_c 较小时, 填料-填料界面的接触热阻不主导总传热阻力, 填料网络形成对最小热阻路径总热阻的影响显著; 当 R_c 较大时, 意味着形成填料网络后会引入极大的接触热阻值, 使网络结构的形成对整体热阻的影响减弱, 从而导致逾渗现象延后甚至消失. 在图 8(b) 中, 在固定接触热阻 $R_c=10^{-7} \text{ m}^2 \cdot \text{K/W}$ 的条件下, 降低界面热阻 R_i 会使逾渗行为愈发明显, 并显著提升逾渗区域的导热增长斜率. 而较大的 R_i 意味着极高比表面积的二维填料与聚合物界面散射严重, 最小热阻路径上始终存在极大地界面热阻, 使得填料网络的演变对总热阻的影响减弱, 从而展现出不明显的逾渗现象. 但是逾渗发生的体积分数区间几乎不随 R_i 的变化而移动. 这表明 R_i 主要影响导热增强的幅度, 而 R_c 主要影响逾渗发生的区间以及导热增长的幅度. 可以

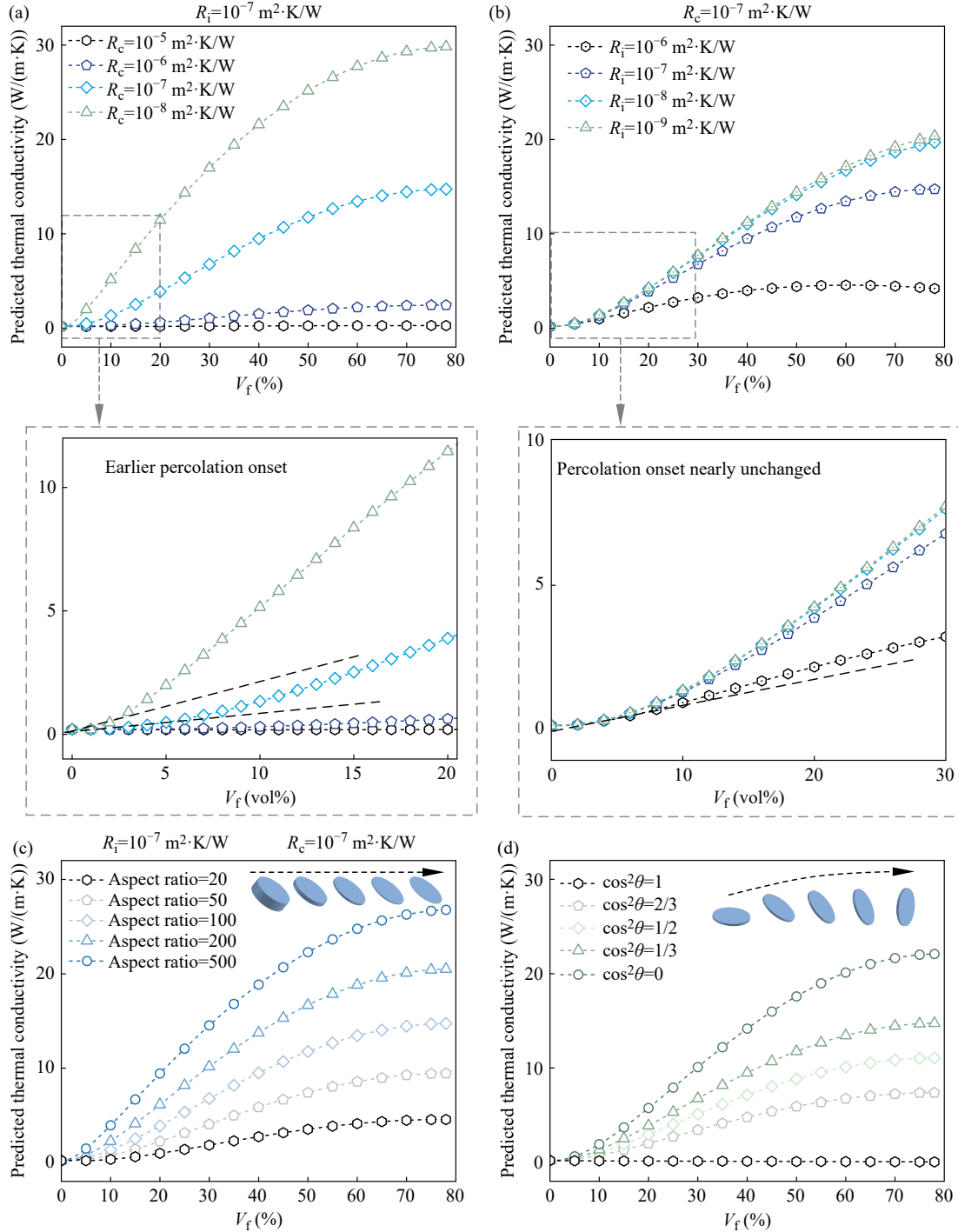


Fig. 8 Influence of key parameters on the percolation behavior of composites. (a) Effect of varying inter-particle contact resistance at fixed interfacial resistance; (b) Effect of varying filler-matrix interfacial resistance at fixed contact resistance; (c) Effect of the filler aspect ratio; (d) Effect of filler orientation within the composite.

理解为, 当首次形成连续通路时, 最小热阻路径的纯聚合物部分清零, 此时最小热阻路径的热阻急剧降低; 此时会引入新的接触热阻 R_c 影响, 若 R_c 较大, 则会削弱贯通网络所带来的热阻降低, 从而使得逾渗现象减弱. 图 8(c) 则固定体系 $R_i = 10^{-7} \text{ m}^2 \cdot \text{K/W}$, $R_c = 10^{-7} \text{ m}^2 \cdot \text{K/W}$, $\cos^2\theta = 1/3$, 改

变填料的长径比为 20~500, 验证结果表明增大长径比可显著提前逾渗区间, 使热导率在较低 V_f 即出现快速增长点. 图 8(d) 在固定填料长径比为 100 的情况下, 考察不同取向度 ($\cos^2\theta$ 从 1 降至 0) 对导热行为的影响. 随着填料由完全水平取向趋于完全垂直取向, 填料排列更有利于沿面外方向

形成贯通通路,从而推动逾渗趋于向低 V_f 区间迁移,并使逾渗区的导热增长斜率进一步增强.由此可见,填料与聚合物的界面热阻、填料与填料间的接触热阻、填料几何尺寸与其取向度协同调控片状填料复合材料的逾渗行为.其中,接触热阻主要决定逾渗阈值的位置,而界面热阻主要影响热导率增强的幅度;同时,长径比的提升以及更有利于形成贯通导热通路的取向结构,能够显著降低逾渗阈值,并强化了逾渗区间热导率的增长速率.上述参数通过对最小热阻路径中各组成热阻的差异化调控,共同决定了复合体系的整体导热性能及其逾渗特征.

3 结论

基于最小热阻路径理论系统构建了一种适用于片状填料聚合物复合材料的导热模型(Platelet-based model).区别于经典导热模型的单个粒子假设,本模型基于连续热阻网络,显示考虑了填料搭接所导致的强相互作用、热流路径的非均匀性及其方向选择性,建立了具有解析可行性的等效热阻网络求解框架,并统一引入填料尺寸、取向

度、界面热阻、接触热阻及体积分数等关键参数,刻画其对面内与面外热传输的耦合影响,实现了有效热导率的统一描述.在跨体系验证中,模型对超200组片状填料复合材料数据的拟合度达到0.98,平均相对误差仅11.54%,预测范围覆盖至50%,成功涵盖目前可加工的主要片状填料体系.此外,验证结果表明,本模型可以通过结构参数捕捉片状填料导热网络的贯通行为与逾渗式增长特征,也能对近线性增长体系与高度取向体系保持稳健预测性能,而不再依赖经验参数;且可为参数反演、导热网络结构设计以及高导热复合材料的可预测开发提供一定的理论基础.从方法层面看,“最小热阻路径理论”作为一种以热流传输路径优化为核心的建模思想,具有进一步拓展至纤维状及杂化填料体系的潜力.未来工作可针对不同填料几何特征和接触形式,对结构单元与热阻构成进行重构;在杂化填料体系中,可将已建立的单一填料导热模型视为等效的传热路径单元,通过路径叠加、权重分配的方式,直接预测整体有效热导率,从而实现对复杂多级导热网络的统一建模与预测.

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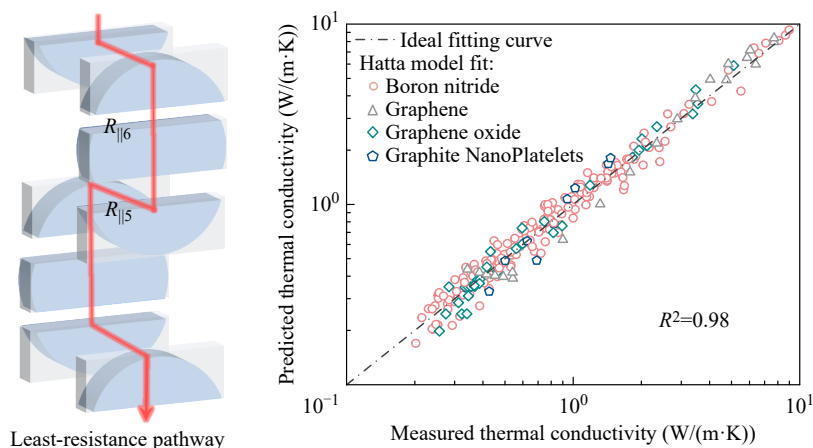
Research Article

Thermal Conductivity Modeling for Platelet-filled Polymer Composites Based on the Least Thermal Resistance Pathway

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Abstract Conventional thermal conduction models based on effective medium theory are typically established under the single-particle assumption, which makes it difficult to capture interparticle interactions arising from reduced filler spacing and the resulting changes in heat-flux directionality. Consequently, these models fail to adequately describe thermal percolation behavior and exhibit pronounced prediction deviations at high filler loadings. To address this limitation, the authors previously proposed a thermal conduction model based on the least resistance pathway theory. By constraining heat flux to propagate preferentially along pathways with the lowest overall thermal resistance, the model enabled accurate prediction of the effective thermal conductivity of highly filled polymer/quasi-spherical filler composites. Building upon this framework, the present study further extends the least resistance pathway concept to platelet-based composites. By equivalently mapping the highly disordered platelet filler distributions with complex spatial correlations into an analytically tractable simplified thermal resistance network, and by introducing a directional selection mechanism inherent to the least thermal resistance path theory, the vectorial nature of heat flux is explicitly captured. As a result, the proposed model effectively describes thermal percolation and anisotropic heat conduction behavior induced by platelet proximity, overlap, and network formation. Validation against experimental data across multiple materials demonstrates that the proposed model achieves a fitting coefficient of 0.98 over more than 200 datasets of platelet-filled polymer composites, with an average relative error of only 11.54%. The predictive capability extends to filler loadings of up to 50 vol%, covering the majority of currently processable platelet-based composites. This model thus provides an efficient and reliable tool for predicting the thermal performance of polymer/platelet filler composites and offers theoretical insight into thermal percolation phenomena in polymer composites.



Keywords Platelet fillers; Polymer composites; Theoretical model; Thermal conductivity; Thermal percolation

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