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Multi-scale modeling of heat conduction in filled polymer composites

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Background

When polymers are modified with granular fillers to increase thermal conductivity, the simultaneous viscosity increase of the composite often limits the allowable filler concentration and thus the achievable thermal conductivity. If fillers from several size classes are smartly combined, the viscosity increase can be mediated, and the allowable filler concentration increased [1,2].
The result is a complex material whose microstructure extends over several orders of magnitude, see Figure 1. The largest particles used may be thousands of times larger than the smallest.
For targeted and efficient material development, it is essential to have precise calculation approaches, that can be used to determine the effective thermal conductivity (ETC) in advance. This makes it possible to reduce time-consuming experimental studies or to investigate material combinations that are not yet physically available.

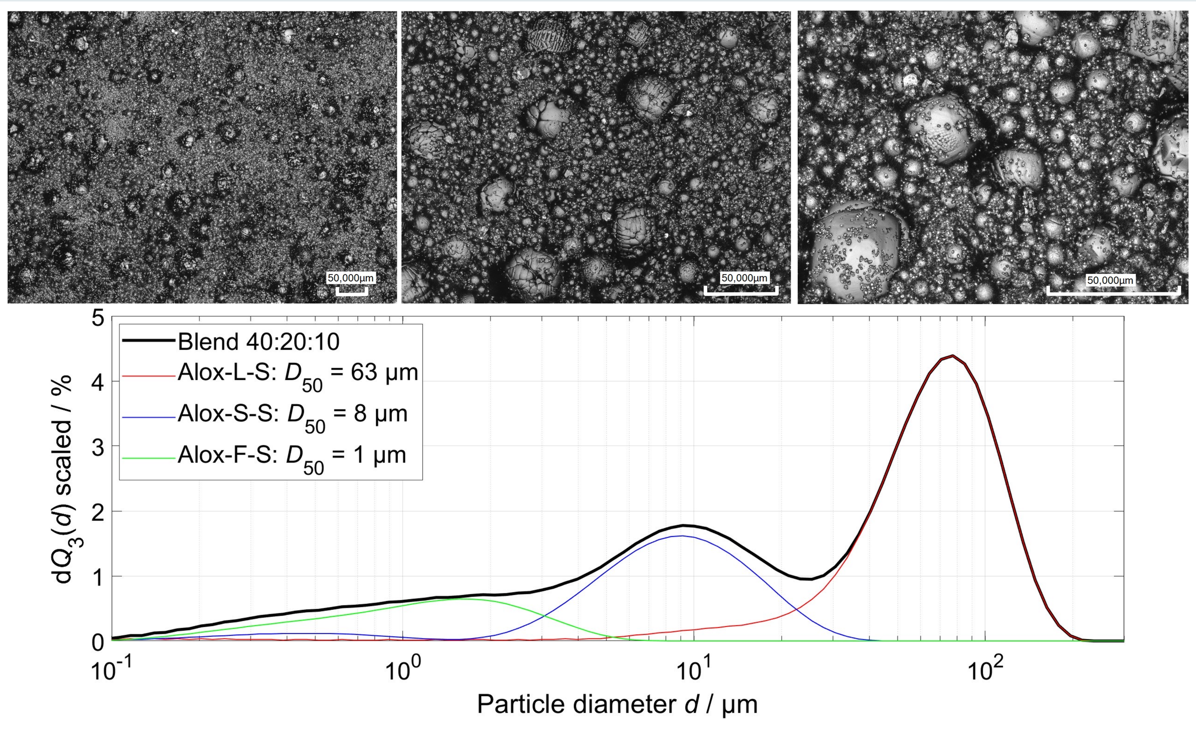


Figure 1: Typical filler blend with three individual alumina grades: Laser microscope images, taken with a Keyence 3D laser scanning microscope VK-X100K and differential distribution of particle sizes, measured using a laser particle sizer Fritsch Analysette 22 NanoTec

Objective and Method

The full-field simulations carried out in [3] and [4] showed that the effective thermal conductivity of filled polymers depends significantly on their microscopic packing structure. A new computational approach is to be designed that on the one hand fully accounts for the microscopic packing effects, but on the other hand overcomes the problem of large scale differences in multi-component filled polymers and thus enables efficient and accurate predictions of the ETC of such filled polymers. For a detailed simulative analysis of the heat transport phenomena in those materials, we have designed a new hierarchical homogenization approach. The individual filler-specific contributions to the increase in ETC are derived from microscopically detailed full-field simulations and then superimposed stepwise. Packing effects in the interfacial transition zones between the filler domains and agglomeration effects are described by additional model extensions.

Modeling approach

1. Microscopically detailed full-field simulations with individual fillers

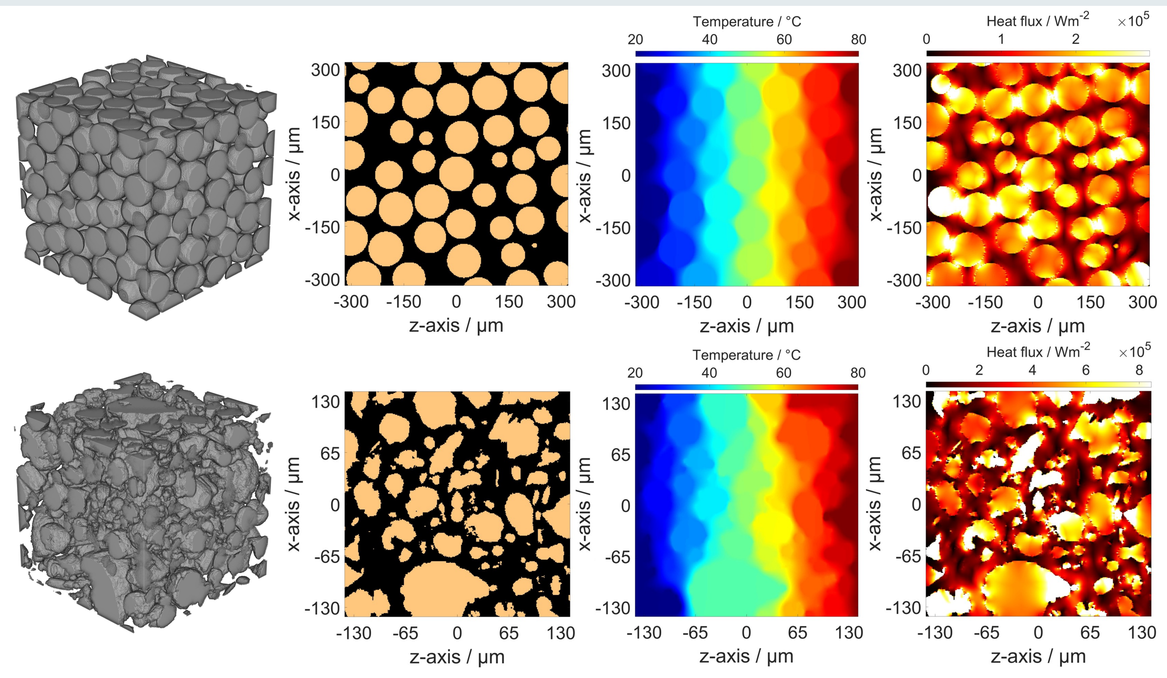


Figure 2: Numerically modeled filler packing in representative volume elements and full field simulation results with a spherical alumina filler (top) and an irregularly shaped aluminum filler (bottom)

2. Dimensionless representation of the results and derivation of a general TC magnification function

Filler loading level
$$\Phi = \frac{\phi}{\phi_{\max}}$$

TC ratio
$$\kappa = \frac{\lambda_D}{\lambda_C}$$

TC magnification
$$\Lambda = \frac{\lambda_{\mathrm{eff}}}{\lambda_C}$$

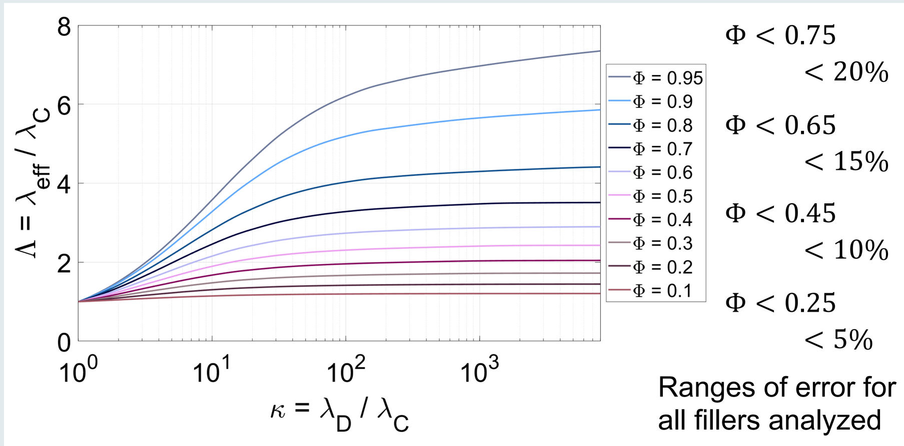


Figure 3: Derived TC magnification function $\Lambda(\Phi, \kappa)$

- Represents almost all packing phenomena in good approximation
  Compaction of the filler packing, Particle size distribution, Particle shape, …
- Takes into account the TC ratio of filler to polymer
- Does not describe agglomeration phenomena

3. Hierarchical homogenization of multi-component filler packings

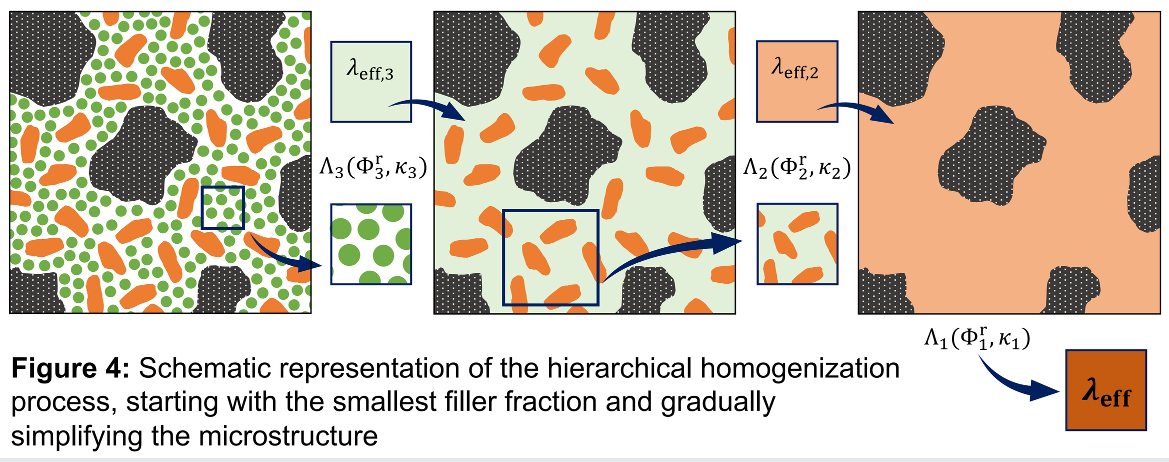


Figure 4: Schematic representation of the hierarchical homogenization process, starting with the smallest filler fraction and gradually simplifying the microstructure

Result: The effective thermal conductivity of the filled polymer

$$\lambda_{\mathrm{eff}} = \lambda_C \prod_{i=1}^{n} \Lambda_i(\Phi_i^r, \kappa_i)$$

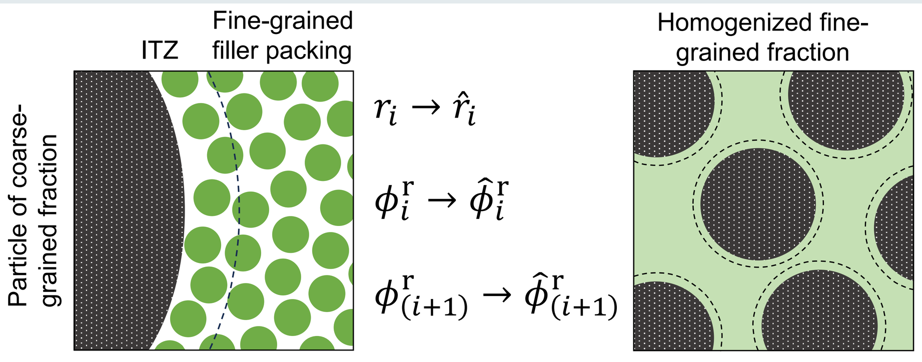
with $\Phi^r = \frac{\phi^r}{\phi_{\max}}$ and $\phi_i^r = \frac{\phi_i}{1-\sum_{k=1}^{i-1}\phi_k}$

Nomenclature

i: Index of filler fraction, with $i = 1, 2, \ldots n$ in descending order of size
ϕ: Filler volume fraction
$\phi_{\max}$: Maximum packing density of filler
ϕ^r: Relative concentration of the fillers in the volume available to them
λ_C: Thermal conductivity of polymer
λ_D: Thermal conductivity of filler particles
λ_{eff}: Effective thermal conductivity of composite

Model extensions

1. Consideration of packing effects at the boundaries between the filler domains
   - Interfacial transition zones (ITZ) between the filler domains
   - Wall effects with impact on the fine-grained packing structure
   - Reduced filler concentration causes reduced conductivity
   - Substitute modeling by adjusted filler volume fraction in fine-grained and coarse-grained filler fraction



i: coarse-grained fraction
$(i+1)$: fine-grained fraction

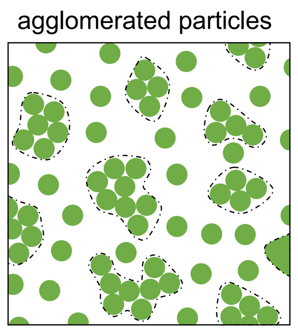
Input from full-field simulations of ITZ

$$\hat{r}_i = f\left(r_i, \lambda_{C,i}, \lambda_{D,i}, \boxed{\lambda_{\mathrm{ITZ},i}, \Delta r_{\mathrm{ITZ},i}}\right)$$
$$\hat{\phi}_i^r = f(r_i, \hat{r}_i, \phi_i^r)$$
$$\hat{\phi}_{(i+1)}^r = f\left(\phi_{(i+1)}^r, \boxed{\left(\frac{V_{\mathrm{ITZ}}}{V_{\mathrm{tot}}}\right)}_{(i+1)}, \boxed{\left(\frac{\phi_{\mathrm{ITZ}}}{\phi_{\mathrm{bulk}}}\right)}_{(i+1)}\right)$$

Figure 5: Model extension for considering interfacial transition zones (ITZ)

2. Consideration of agglomeration in the individual filler domains
   - Agglomeration causes local, efficient heat paths and increases the effective thermal conductivity in general
   - Implementation of a sub-homogenization step

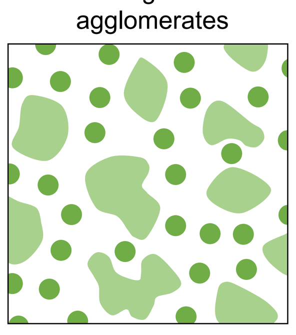
Domain with loose and agglomerated particles



Level of agglomeration
$$\psi = \frac{V_{\mathrm{D,aggl.}}}{V_D}$$

$$\phi_{\psi,i}^r = \phi_{\max,i}$$
$$\Phi_{\psi,i}^r = 1$$
$$\lambda_{\mathrm{eff},\psi,i} = f(\lambda_C, \lambda_{D,i})$$

Homogenized agglomerates



$$\phi_{(1-\psi),i}^r = f(\psi, \phi_i, \ldots \phi_{\max,i})$$
$$\Phi_{(1-\psi),i}^r < \Phi_i^r$$
$$\lambda_{\mathrm{eff},(1-\psi),i} = f(\lambda_{C,i}, \ldots \lambda_{D,i}, \Phi_{(1-\psi),i}^r)$$

Homogenized continuous phase

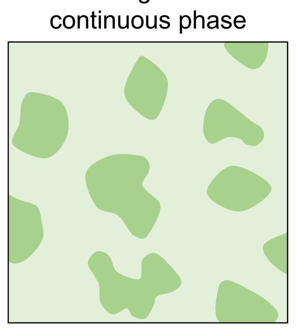


Figure 6: Model extension for considering agglomeration of the individual filler fractions

Experimental validation

- Fabrication of various polymer composites
- Measurement of thermal conductivity using the steady-state cylinder method according to ASTM D5470
- 265 composites in total
- Polymer: Epoxy SikaBiresin® TD150+TD165
- Fillers of aluminum, alumina, silica, and aluminum hydroxide
  - in spherical and irregular shape
  - D_{50} between 0.8 µm and 150 µm
- Binary, ternary, quaternary blends
- $\phi = 0.40 \ldots 0.77$

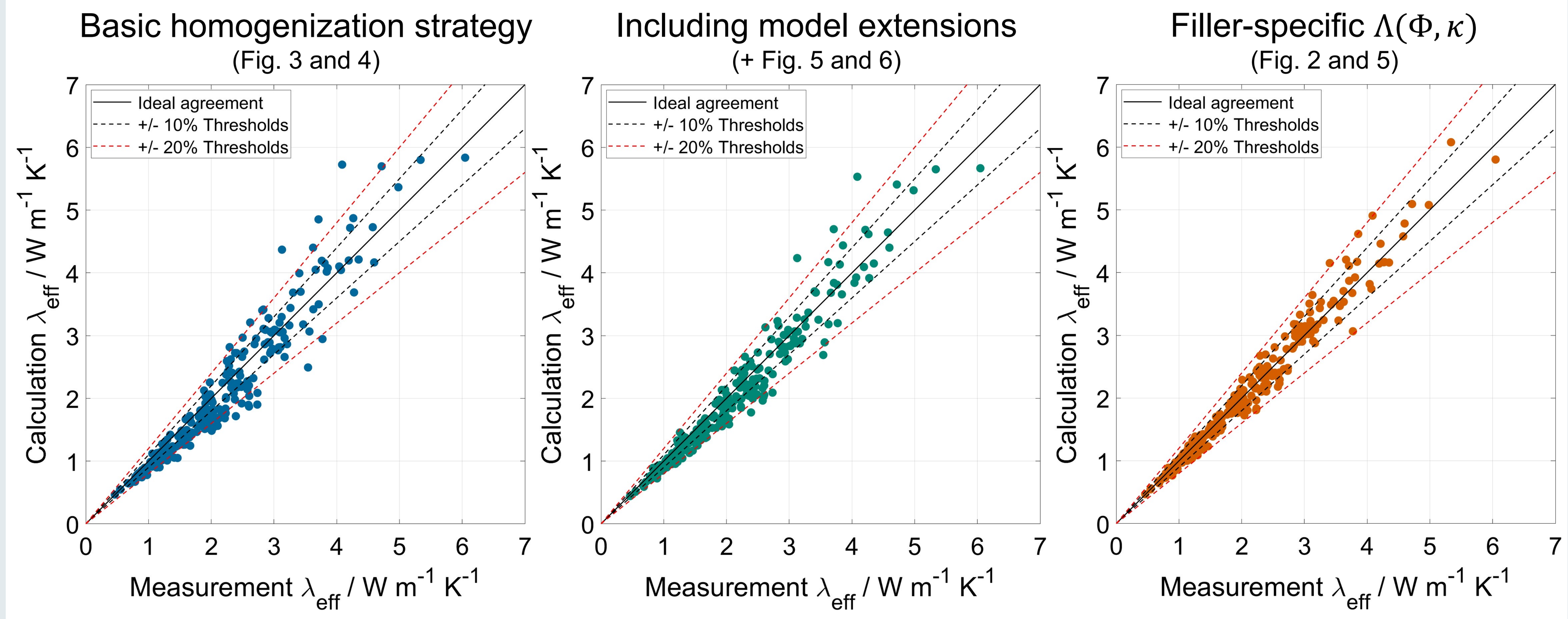


Figure 8: Comparison of calculated effective thermal conductivities with measured thermal conductivities for different calculation approaches. Data points: Samples; Solid lines: Reference for ideal agreement with $\lambda_{\mathrm{eff}}^{\mathrm{calc}} = \lambda_{\mathrm{eff}}^{\mathrm{meas}}$; Dashed lines: Thresholds for +/- 10% and +/-20% deviation of calculated λ_{eff} from measured values.

Average deviations	11.2 %	8.9 %	4.9 %
95 % of the calculations are more accurate than	24.5 %	19.4 %	14.2 %

Application: Systematic formulation studies

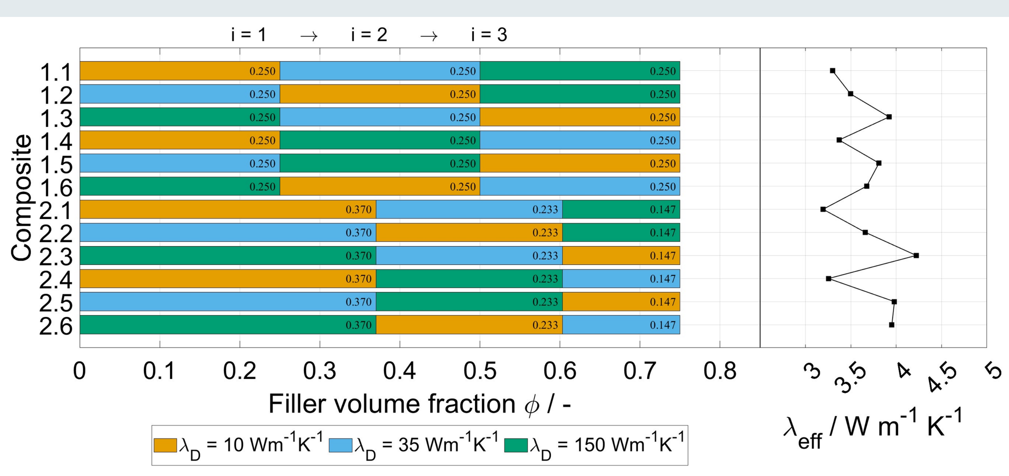


Figure 7: Composition and calculated ETC of fictitious ternary composites

- Ternary filler mixture with materials of different thermal conductivity
  - $\lambda_{D,A} = 10\ \mathrm{W\,m^{-1}\,K^{-1}}$, e.g. aluminum hydroxide
  - $\lambda_{D,B} = 35\ \mathrm{W\,m^{-1}\,K^{-1}}$, e.g. alumina
  - $\lambda_{D,C} = 150\ \mathrm{W\,m^{-1}\,K^{-1}}$, e.g. aluminum nitride
- Clear result: The potential of higher thermally conductive fillers is only fully exploited in the coarse-grained fraction

Conclusion and Outlook

- Successful development of a hierarchical homogenization approach for ETC predictions of multi-scale filled polymers
- Findings from detailed, filler-specific full-field simulations can be integrated
- Very good agreement with experimental results, deviations only in the order of magnitude of the measurement uncertainty
  - 11.2 % with the basic homogenization strategy
  - 8.9 % with the model extensions for ITZ and agglomeration
  - 4.9 % with filler-specific TC magnification functions
- Possible application: Systematic formulation studies and optimization of filler blends
- It is planned to optimize the calculation approach with the direct use of microscopic full-field simulations to describe the effects in the ITZ

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