Size Effects in Computational Homogenization of Polymer Nano-Composites

Paras Kumar1,2,* and Julia Mergheim1

1 Chair of Applied Mechanics, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany
2 Central Institute for Scientific Computing, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany

Nano-particles, as compared to micro-sized inclusions, result in a much better improvement to the mechanical properties of otherwise brittle polymers. Standard first-order computational homogenization lacks the length scale necessary to capture this size effect. In this work, a computational homogenization scheme enhanced with interface energetics is considered and its applicability to polymer nano-composites with different types of filler particles is assessed through systematic numerical experimentation. The study reveals that the method performs quantitatively much better in the case of softer inclusions as compared to the case where the inclusions are much stiffer than the matrix material, which happens in the case of silica nano-particles.

1 Introduction

Experimental evidence reveals nano-sized reinforcements to be more effective than micro-sized filler particles in terms of their ability to improve the mechanical behavior of otherwise brittle polymers [1]. The formation of an interphase layer around the filler particle, which is prominent in the case of nano-particles due to their much higher specific surface area (SSA), has drastic effects on the overall properties of the composite material [2]. Standard continuum-mechanics-based models, due to the absence of a necessary length scale, cannot capture this size effect and thus appropriate enhancements are needed.

In this work, we consider a modification of the standard first-order computational homogenization scheme, wherein the interface between the matrix and the filler materials is equipped with its own energetic structure. The next section summarizes the overall working principle of the approach. A detailed mathematical exposition on the topic of interface energetics and its application to homogenization can be found in [3, 4] and the references therein.

2 Interface-Energetics-Enhanced Computational Homogenization (IECH)

The fundamental idea of this approach is based on the concept of lower dimensional energetics. Herein, similar to the bulk, lower dimensional physical entities, such as interfaces between two materials, are equipped with their own specific strain energies [3]. Furthermore, the kinematic quantities (denoted as \{\dot{\bullet}\}) at any point on the interface are obtained through projection of their bulk counterparts (denoted as \{\bullet\}) by means of a second-order projection tensor given by \(\mathbf{\Pi} = \mathbf{I} - \mathbf{N} \otimes \mathbf{N}\), where \(\mathbf{N}\) denotes the unit normal to the interface in material configuration (see Figure 1) and \(\mathbf{I}\) is the second-order unit tensor. Neglecting the body forces, the balances of linear momentum including contributions from the bulk \(B_0\) and the interface \(I_0\) are given as

\[
\text{Div} \mathbf{P} = 0 \quad \text{in} \quad B_0, \\
\text{Div} \mathbf{\Pi} + [\mathbf{P}] \cdot \mathbf{N} = 0 \quad \text{on} \quad I_0, 
\]

with the assumption that the interface is elastic, i.e. \(\varphi = 0, [\mathbf{P}] \cdot \mathbf{N} \neq 0\). Here, \(\mathbf{P}\) and \(\mathbf{\Pi}\) represent the Piola stress for the bulk and the interface, respectively.

The inclusion of interface energetics in the computational homogenization scheme leads to an extended Hill-Mandel condition, and, consequently, the macroscopic Piola stress \(\mathbf{P}^M\) is computed as

\[
\mathbf{P}^M = \frac{1}{|B_0|} \int_{B_0} \mathbf{P} \, dV + \frac{1}{|I_0|} \int_{I_0} \mathbf{\Pi} \, dA = \frac{1}{|B_0|} \int_{B_0} \mathbf{P} \, dV + \frac{|I_0|}{|B_0|} \int_{I_0} \mathbf{\Pi} \, dA = \mathbf{P}_{|B_0|} + \frac{1}{|I_0|} \frac{|I_0|}{|B_0|} \int_{I_0} \mathbf{\Pi} \, dA \tag{2}
\]

where \(|B_0|\) and \(|I_0|\) represent the volume of the RVE and the surface area of the interface, respectively. Thus, this approach includes the length scale \(S_I\) which allows us capture the size effect as explained below with the help of numerical examples.

* Corresponding author: e-mail paras.kumar@fau.de, phone +49 9131 85-20323, fax +49 9131 85-28503

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
3 Numerical Results and Discussion

Firstly, the RVE of Figure 1 has an initial length scale $S_0^1$. Now, if we reduce the size of the RVE by a factor $1/K$, its length scale changes to $S_1$, while keeping the volume fraction of the filler material constant, yielding $S_0^2/S_1 = 1/K$. We consider an epoxy matrix ($\mu_E = 1185\,\text{MPa}, \nu_E = 0.35$) with two different filler materials, rubber ($\mu_R = 0.67\,\text{MPa}, \nu_R = 0.49$) and silica ($\mu_S = 34\,188\,\text{MPa}, \nu_S = 0.17$). The model is tested for three different loading conditions: (i) uni-axial tension, (ii) shear and (iii) volumetric loading. The variation of shear modulus $G$ for different values of the interface shear modulus $\bar{\mu}$ is shown in Figure 2 for the two filler materials considered in this study. For the sake of brevity, only the results for uni-axial loading are presented here. The results for other loading scenarios show a similar pattern. The value $\bar{\mu} = 0$ corresponds to a perfect interface, which is the case for the standard homogenization approach.

Referring to Figure 2a, with the increasing stiffness of the interface, the overall response of the RVE becomes stiffer as the filler particles become smaller. The size effect becomes pre-eminent for the cases where $\bar{\mu} \geq \max\{\mu_m, \mu_f\}$. Furthermore, the size effect appears to saturate as the particle size reduces further. This saturation is more prominent for the case of silica filler particles as depicted in Figure 2b. It is noteworthy that the degree of stiffening achieved is highly sensitive to the relative stiffness between the matrix and the filler regions, re- 

![Fig. 1: A 2D RVE comprised of the matrix material (shown in blue) and a circular inclusion (shown in red). Here, the subscripts $m$ and $f$ refer to the matrix and the filler regions, respectively.](image)

![Fig. 2: Variation of the macroscopic Piola stress with relative length scale, for the uni-axial tensile loading scenario.](image)

4 Outlook

The above discussion reveals the limitation of the interface energetics approach in modeling the size effect in the case of polymer nano-composites containing silica nano-particles. As an alternative to the present approach, modeling of a finite thickness interphase with mechanical properties grading across the interphase is being explored.

Acknowledgements This research was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - 377472739/GRK 2423/1-2019. The authors are very grateful for this support. Open access funding enabled and organized by Projekt DEAL.

References

[1] Cho J. and Joshi M.S., Composites Science and Technology 66:1941-1952, 2006.
[2] Schmidt D., Shah D. and Giannelis E. P. Current Opinion in Solid State and Materials Science 6:205-212, 2002.
[3] Javili A., McBride A. and Steinmann P. Applied Mechanics Reviews 65(1):2013.
[4] Javili A., McBride A., Mergheim J., Steinmann P. and Schmidt U. International Journal of Solids and Structures 50:2561-2572, 2013.