Multi-Scale Modeling of Polymer Nanocomposites

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ABSTRACT

Mean-field (MF) homogenization describes composite behavior based on average stress/strain tensors on phase and composite level and combines analytical formulae with numerical simulation. MF can handle coated inclusions, which is important for nanocomposite modeling because the coating properties can emulate the force between nano-particles. Also for matrix-particle interaction, the coating can represent a real, new phase, e.g. matrix material with density variations. Two-level homogenization is applied to densely packed clusters of particles and voids. To verify MF predictions, realistic FE models are constructed representing microstructure geometry, including cluster size distribution from image analysis. The MF predicted stiffness, obtained in seconds, are less than 5% off the FE predicted stiffness, obtained in hours. In FEA, the coating can represent electron tunneling and percolation, increasing composite conductivity with many orders of magnitude. Results are compared with experimental data from industrial partner.

Keywords: nanocomposites, multi-scale, microstructure, mean-field homogenization, finite element analysis, micromechanics

1 INTRODUCTION

1.1 Nanocomposite modeling

Due to the small size of nano-inclusions, their surface becomes an important factor determining the composite properties. For "microcomposites" (with inclusions larger than one micron) it is often sufficient to consider the phases' bulk properties, while for nanocomposites enhanced modeling is needed to capture this surface effect, or other "nano-effects". Due to these nano-effects, it is possible to obtain a given improvement of matrix properties (mechanical, electrical, thermal, ...) with a much smaller filler weight fraction (thus with a lower cost), raising the interest of manufacturers. Mineral nano-scale inclusions are provided as a powder of particles with average size 5–150nm. During production, nano-filler is dispersed in the matrix. Full dispersion is rarely reached and clusters of nano-filler appear. Clustering can be advantageous, e.g. when clusters of densely packed nano-particles have the same stiffness as a solid micron-sized inclusion, while using less filler material. This beneficial use of voids in between particles induces great property enhancements.

2 MEAN-FIELD HOMOGENIZATION

Mean-field (MF) homogenization techniques [1] describe the composite rheological behavior based on the average stress and strain tensors on phase level and on composite level. These analytical formulae are applied in a numerical simulation.

2.1 Multi-level homogenization

This MF approach is successful for a wide range of composites and can also handle coated inclusions, which is important for nanocomposites because the nano-particles interact with other nano-particles and with the matrix. For matrix-particle interaction, the coating represents a real, new phase ("interphase"), e.g. matrix material with density and stiffness variations. For particle-particle interaction, the coating properties emulate the force between particles. While MF analysis is size-independent, it is possible by "design of experiment" to obtain curves representing the size-effect, i.e. the effect of coating thickness for a given particle size. All the MF results presented further have been obtained with the Digimat-MF © software [2].

In the MF approach, the problem of a composite with coated inclusions can be seen as a three phase composite. The best suited method to homogenize this multi phase composite is a multi-level approach: the inclusions are first homogenized with their coatings (first level of homogenization), and the resulting material, which can be seen as an “effective inclusion”, is then homogenized with the matrix (second level of homogenization) (see Figure 1). This approach has been applied to a composite reinforced with spherical nano-particles, where coatings are used to model the interphase. Results are presented in Figure 2 and show that it is possible to model, to some extent, size

effects with a MF approach. For a given coating thickness, the composite properties are varying when the inclusion size changes.

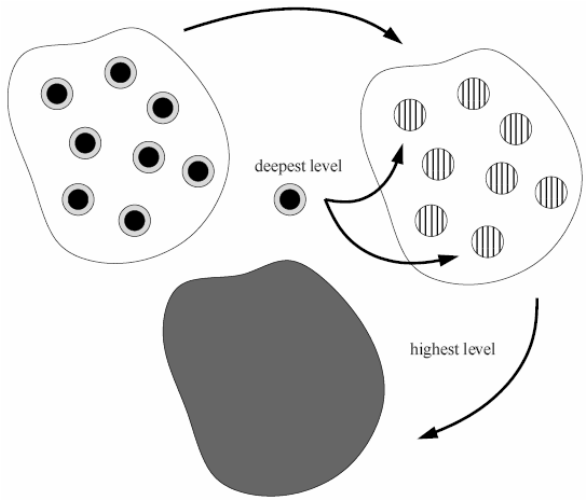

Figure 1: Multi-level homogenization

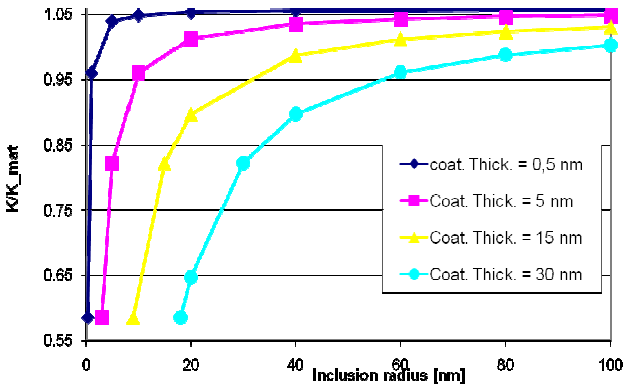

Figure 2: Multi-level method applied to a matrix reinforced with spherical coated nanoparticles. The four curves have been obtained for four different coating thicknesses. The curves show the ratio between the bulk modulus of the composite and of the matrix as a function of the inclusion radius. Matrix material: E=0.9 GPa and ν=0.35. Coating material: E=0.45 GPa and ν=0.35. Inclusion material: E=20.4 GPa and ν=0.16.

2.2 Effective particle

Figure 3 shows a SEM image of PC+$BaSO_4$ nanocomposite. In this micrograph, one very large and dense cluster can be found in the upper left region, while most other inclusions are quite evenly dispersed. If we look at a larger region, some other large clusters like this one can be found. A closer look at these clusters shows that there is no matrix in between the inclusions inside the cluster, just voids.

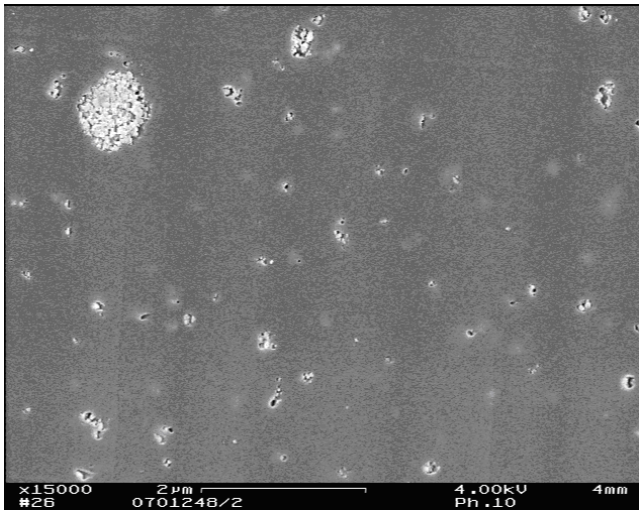

Figure 3: Nano inclusion SEM images. A very large cluster can be found in the upper left region, while all other inclusions are quite well dispersed.

A similar, two-level approach can also be used for this kind of densely packed clusters: nano-filler is first homogenized with the voids in the cluster, and the resulting "effective cluster material" is homogenized with the matrix. Knowing the shape of the elementary inclusions, and using simple geometrical considerations, it is possible to get a good estimate of the fraction of voids in the cluster. For example, for densely packed spherical inclusions with random packing, the maximum packing density is about 64%, which means 36% of voids in the cluster. This first step of homogenization leads to an "effective particle", which can be reused for further homogenization steps.

2.3 Experimental validation

Experimental results obtained on two different composites are presented in Table 1 and compared to the MF results for validation. The third column shows the moduli obtained with MF without taking into account the nano effects (i.e. particle-particle interaction modeled as a coating and densely packed cluster modeled with an effective cluster material). The fourth column shows the moduli obtained with MF with nano-effects taken into account.

Composite	modulus from experiment	modulus from MF	modulus from MF +nano-effects
PC+6% BaSO4	2480 MPa	2269 MPa (-9%)	2415 MPa (-3%)
PC+15% BaSO4	2729 MPa	2398 MPa (-14%)	2793 MPa (+2%)

Table 1: Comparison between Digimat-MF predictions and experimentally measured Young Modulus.

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3 FINITE ELEMENT ANALYSIS OF MICROSTRUCTURES

Another way to verify and complement the MF predictions is to use detailed FE models of the studied microstructures. Models and results are presented for polymer matrix with mono- and poly-dispersed nano-filler, including coating, clustering and using a cluster size distribution as determined from image analysis. The MF predictive modulus, obtained in CPU-seconds, are less than 5% off the modulus predicted by FE , obtained in CPU-days. FE analysis reveals that clustering of particles may increase the maximum stress in the matrix by 25%.

3.1 Influence of particle clustering

Four different RVE of PC-$BaSO_4$ have been generated using Digimat-FE to study the influence of clustering and particle interactions. Digimat-FE is one tool of the Digimat software platform [2] that performs random RVE generation based on microstructural parameters. Once a RVE has been generated by Digimat-FE, it can be exported to a FE package, and the finite element model, with material assignement, definition of boundary conditions, etc is built in a fully automatic way. In this study, we used Abaqus/Standard as the FE solver and Abaqus/CAE as preprocessor.

All four RVEs have more or less 40 $BaSO_4$ spherical inclusions with constant size, and the total volume fraction of inclusions is 5%. When a coating is used to model the interphase, the total volume fraction of this coating is 4%. An example of a RVE generated by Digimat-FE and meshed with Abaqus/CAE is shown in Figure 4. A cut view of the stress field at the end of a uniaxial tensile test is shown in Figure 5. The coatings and the stress concentrations that build up between neighboring inclusions are clearly visible. For each RVE, three uniaxial tensile test have been simulated, one in each principal direction, and the three corresponding Young moduli (E_x,E_y and E_z) have been computed. The results of these FE analysis are presented in Table 2 and compared to the MF predictions. For the four RVE, the anisotropy (maximum relative difference between the three Young moduli) is quite limited, which is a sign that the simulations are accurate enough. The agreement between the MF and FE results is quite good. That shows that the effect of particle clustering on the macroscopic Young modulus is quite limited. However, particle clustering has a much larger effect on the maximum matrix stress (see Figure 5).

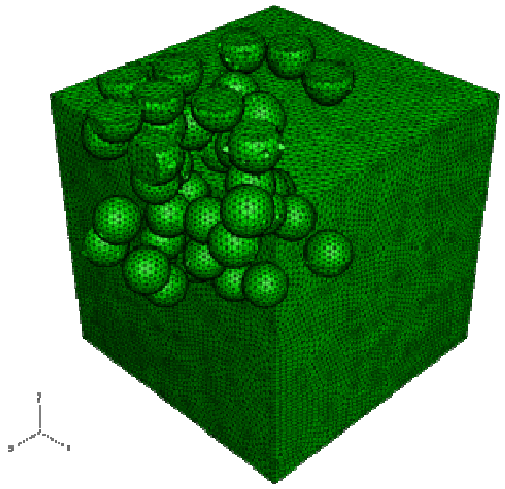

Figure 4: RVE2, ±40 inclusions in one cluster

RVE	FEA Young modulus MPa	Young modulus anisotropy %	difference with MF %	Number of inclusions	FEA model size Number of nodes	FEA CPU time sec
1 Coating/no cluster	2712	1.1	0.7	40	986,853 (2nd order)	50,924 (2nd order)
2 Coating/Cluster	2842	3.3	2.5	40	1,098,338 (2nd order)	56,677 (2nd order)
3 No Coating/No cluster	2576	1.64	3.9	37	20,313 (1st order)	111 (1st order)
4 No Coating/Cluster	2604	0.15	4.4	60	20,054 (1st order)	107 (1st order)

Table 2: Summary of the FE results and comparison to MF results. The FEA Young modulus is the average of the Young modulus computed in the three principal directions. Young modulus anisotropy is the maximum relative difference between the Young moduli in the three principal directions. RVE1 and RVE2 uses coating to represent the intephase, RVE1 is without clustering and RVE2 with one cluster. RVE3 and RVE4 are without coating, RVE3 without clustering and RVE4 with one cluster.

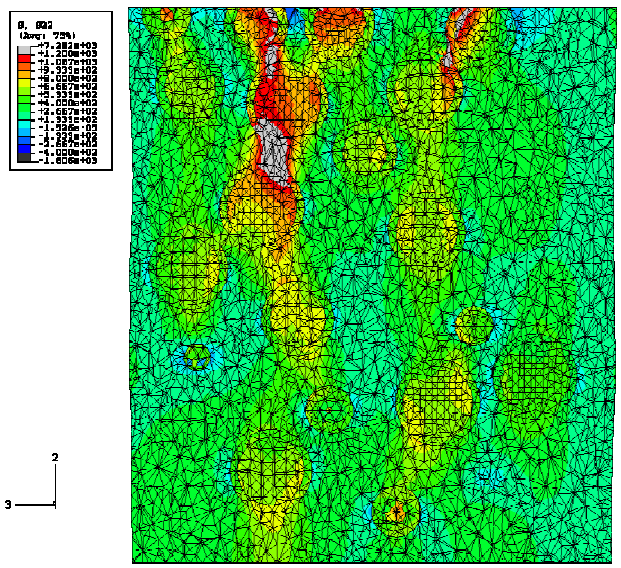

Figure 5: RVE2: Stress field (S22 component) after a uniaxial tensile test. The stress concentrations between neighboring inclusions are clearly visible.

3.2 Influence of particle size distribution

An experimental inclusion size distribution has been obtained from images of real microstructures (see Figure 3), with an image analysis software, ImageJ [4]. This size distribution has then been used to generate a RVE with an inclusion phase following this size distribution. The resulting RVE is shown in Figure 6.

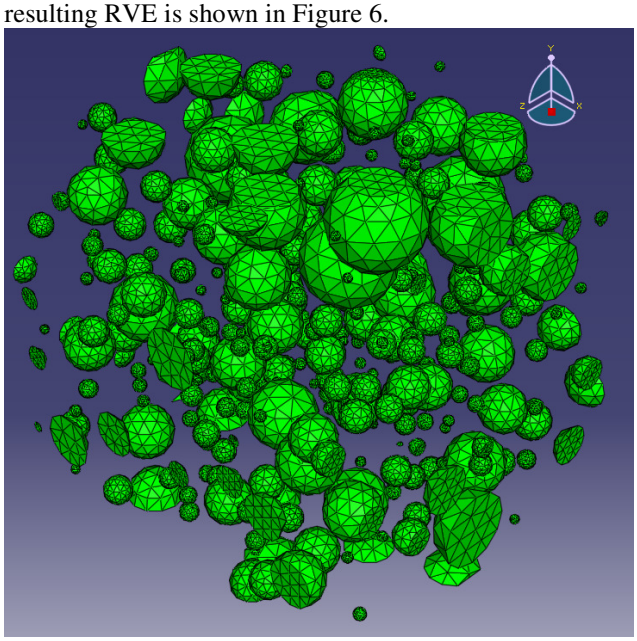

Figure 6: Randomly generated RVE (328 inclusions) of PC + $BaSO_4$ (13.7% vol). For clarity, only the inclusion phase is shown.

The same three uniaxial tensile tests have been simulated on this RVE. The computed Young moduli are the following:

E_x = 2828 MPa
E_y = 2830 MPa
E_z = 2811 MPa

The anisotropy is once again very small (around 0.4%). Using Digimat-MF for the same material, we computed a Young modulus of 2692 MPa (4.7% difference w.r.t. FE results). This shows that the influence of the particle size is real, but not so important when looking only at the predictions of the Young modulus. However, we can expect the influence of particle size distribution to be much bigger in the non linear regime. In this case, the MF approach might not be accurate enough and it might be necessary to rely entirely on detailed FE models.

4 CONCLUSION

Modeling of nanocomposites using a MF approach was demonstrated. Using particular modeling techniques like multi-level homogenization, coated inclusions to model interactions, and effective cluster material, it is possible to get accurate predictions of elastic constants of nanocomposites. These predictions are obtained in a few seconds on a regular desktop computer.

The modeling techniques were validated by comparison to experimental data and to results of detailed FE simulations on several models. This confirmed that a MF approach can successfully predict elastic constants, but that FE models of large, realistic RVE are required when more detailed information is seeked, like the maximum stress, the location of stress concentrations,…

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