DIGIMAT for

NANO-COMPOSITES

Document Version 2.0.1, February 2010

info@e-Xstream.com www.e-Xstream.com

Materials: Engineering Plastics, Reinforced Plastics, Mineral and Clay fillers.
e-Xstream Technology: DIGIMAT, Digimat-MF, Digimat-FE.
Complementary CAE Technology: Abaqus/Standard
Industry: Material Suppliers, Automotive, Consumer Products.
Capabilities: modeling mechanical, thermal and electric properties of composites with nano-scale fillers, including nano-effects such as

- Representing the interfacial zone between matrix and filler,
- Size effect: absolute filler size, absolute coating/interface thickness,
- Clustering of filler, taking into account the size distribution of clusters,
- Interaction between filler particles,
- Percolation,
- Use of an "effective particle" to represent relevant nano-filler properties.

Case Study: Prediction of composite modulus for a Polycarbonate (PC) matrix reinforced with mineral nano-filler.
Related document:
DIGIMAT Brochure
DIGIMAT for ENGINEERING PLASTICS

TABLE OF CONTENT

EXECUTIVE SUMMARY

e-Xstream engineering is a software and engineering services company, 100% focused on advanced material modeling technology. We help our customers reduce their development costs and the time needed to bring innovative and high-quality products to the market. For a general introduction to the DIGIMAT software suite, please refer to the DIGIMAT product sheet. Here we will limit ourselves to topics particular to nanocomposites, i.e. composites with nano-size filler particles.

As the DIGIMAT software suite is dedicated to the modeling of composite materials in a broad sense, extended functionality has been added specifically for "nano-effects", i.e. effects particular to nanocomposites:

- Interface between matrix and nano-filler
- Size effect: absolute filler size, absolute coating/interface thickness
- Clustering and size distribution of clusters
- Interaction between filler particles
- Effective particle

Depending on the composite specifications, some or all of the nano-effects mentioned above may be of importance. These nano-effects are explained in detail in the section below, "Modeling Nanocomposites with Digimat-MF". The special modeling features are demonstrated by means of an industrial Case Study for a nanocomposite with PC matrix and mineral (barite) nano-filler, including a Digimat-MF and Digimat-FE analysis.

Digimat-MF and Digimat-FE are complimentary tools, also for nanocomposites modeling. Digimat-MF, based on nonlinear semi-analytical homogenization theory offers accurate and efficient predictions at the macroscopic scale (i.e. composite level). The results at the microscopic scale (i.e. for the constituent phases) are averaged. Digimat-FE, based on direct nonlinear Finite Element Analysis (FEA) of a material Representative Volume Element (RVE), offers accurate predictions at the macroscopic and local microscopic scales. The time needed to build and solve a Digimat-FE model is much larger than for Digimat-MF. The software and technology are backed up by a team of engineers with a strong expertise in nonlinear finite element analysis, material modeling and multi-scale analysis of reinforced plastics.

MODELING NANOCOMPOSITES WITH DIGIMAT-MF (MEAN FIELD HOMOGENIZATION TECHNIQUES)

Digimat-MF is a user-friendly micromechanical material modeling software where the user specifies the material behavior of the phases, the microstructure morphology and the loading applied to the composite material. Digimat-MF then predicts the composite’s mechanical, thermal, thermomechanical and electrical behavior based on homogenization techniques (Mori-Tanaka or Interpolative Double Inclusion models. Filler particles are assumed to have an ellipsoidal shape defined by the aspect ratio (AR = Length/Diameter). This way, spherical particles, platelets and fibers can be modeled correctly, while even for non-ellipsoidal particles (such as a stack of clay sheets) accurate results are obtained. One or more phases of inclusions can be defined, e.g. regular glass fibers and mineral nano-filler in a polymer matrix.

DIGIMAT is a software platform aimed at modeling composite materials. The following capabilities extend the DIGIMAT functionality towards modeling "nano-effects", i.e. effects particular to nanocomposites:

- **Interface between matrix and nano-filler**

  Often the nano-filler is coated with a chemical agent, e.g. a surfactant to promote particle dispersion during processing. Even for uncoated nano-filler, the properties of the matrix-particle interface (i.e. the contact zone between the particle's surface and the matrix material) may be altered significantly, e.g. because of density variations due to polymer chain alignment, or because of polymer crystallization at the surface of a clay nano-sheet. In such cases, Digimat-MF allows the user to define a coating around the nano-particle, with specific thickness (absolute or relative, see below) and properties. In the Multi-Level scheme (Figure 1), the nano-particle is homogenized first with its coating, and this result (called the "effective particle") is then homogenized with the matrix material. The coating feature can also be used to reverse-engineer the properties of the particle-matrix interface from experimental data obtained on the composite.

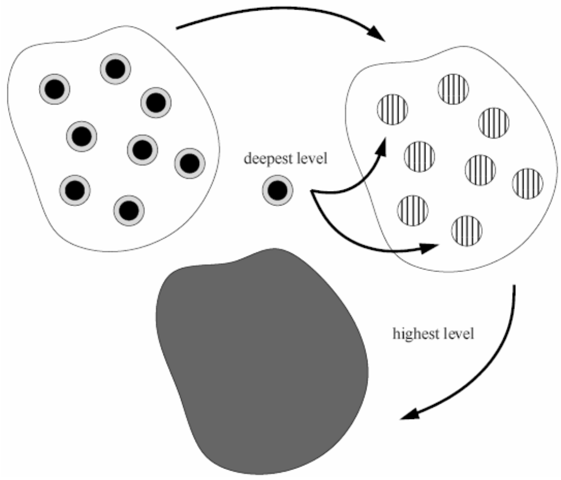


Figure 1: Principle of **Multi-Level homogenization**: the inclusions (black) are first homogenized with their coating (grey) to give an "effective particle", which in turn is homogenized with the matrix (white) to give the composite material (dark grey).

- ## Size effect

Digimat-MF homogenization techniques do not consider an absolute filler size but only use the filler's aspect ratio (constant, or in the form of a distribution) and the filler mass or volume fraction. However, in reality, the interface between matrix and nano-particle (or the coating of the particle) may be defined by an absolute thickness. Digimat-MF offers the opportunity to define the absolute interface/coating thickness along with an absolute particle size. Figure 2 below depicts the dependence of the material stiffness on the absolute filler size.

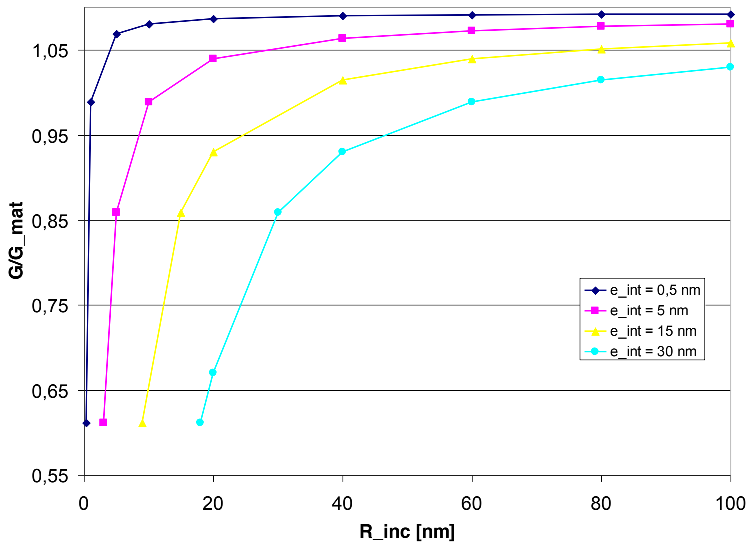


Figure 2: **Size effect**: the ratio of composite shear modulus over matrix shear modulus G/G_{mat} depends on the particle radius R_{inc} and on the coating (matrix-particle interface) thickness e_{int}.

- ## Clustering and size distribution of clusters

While processing the nano-composite, a lot of effort is required to obtain a high degree of dispersion of the nano-particles in the matrix. Here, "fully dispersed" means that all particles have been separated from each other. In reality, nano-particles often remain "clustered" (Figure 3) in groups of a few or many thousands of particles.

For clusters that consist of densely packed particles with (almost) nothing but voids in between, an "effective cluster material" can be defined as the result of the homogenization of the particles and the voids. This effective cluster material can then, in turn, be homogenized with the matrix (Figure 4). This two-level homogenization is done automatically in Digimat-MF using the Multi-Level scheme.

The size distribution of the clusters can be taken into account when using Digimat-FE, see below.

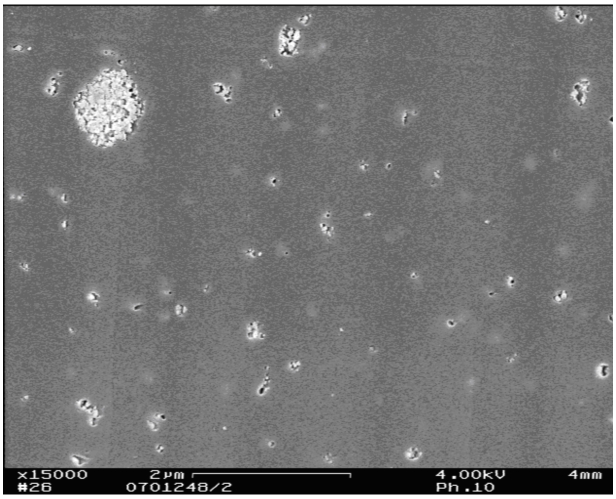


Figure 3: Micrograph (SEM) of the nano-composite microstructure, revealing **single particles** as well as large **clusters**.

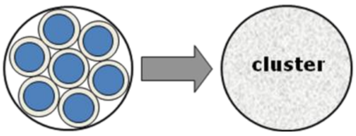


Figure 4: Nanoparticles (perhaps with coating) that are packed in a dense cluster with voids are homogenized into an **"effective cluster material"** that takes all relevant properties into account.

- ## Interaction between filler particles

Apart from the matrix-particle interface, it may be needed to model the particle-particle interaction as well. As the particles are nano-sized, their surface may attract (or repel) neighboring particles, e.g. due to molecular Van der Waals forces, stereoscopic effects or chemical agents (coating). In Digimat-MF this particle-particle interaction can be represented by a coating around the particle, with stiffness properties that emulate the interaction. This representative coating is then homogenized with the particle itself, and the resulting effective particle is used for further steps, e.g. homogenizing the effective particles with voids to form an effective cluster material.

- ## Effective particle

Some or all of the nano-effects described above may occur, depending on the specifications of the nano-composite. In many cases it is necessary to represent these nano-effects by a new phase (e.g. a coating around the particle) with material and phase properties that emulate the physics of the relevant nano-effects. This new phase is then homogenized with the original particle phase to produce a phase with effective properties, called the "effective particle". For example, for a clay nano-composite, the effective particle may be the integration of a stack of clay sheets and the inter-sheet interactions (Figure 5), taking all relevant dimension and properties into account. The correct determination of the appropriate volume fraction of this "effective particle" is essential for reliable nano-composite modeling.

Digimat-MF offers the design engineer all necessary tools to compute the mechanical properties of the effective particle and to use this in subsequent steps of the analysis.

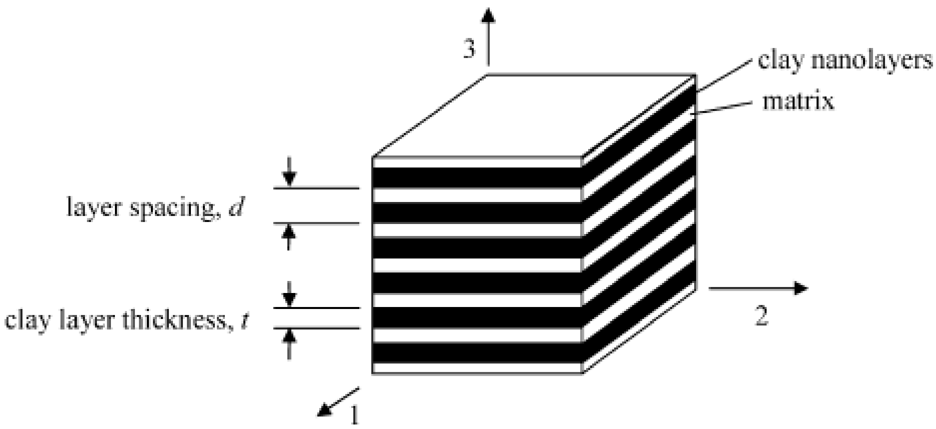


Figure 5: A stack of clay nano-sheets (black) with matrix material in between (white), form the "effective particle" for a class of **nano-clays** (taken from [Sheng] Polymer 45 (2004) p.487).

- ## Percolation

When studying the electrical conductivity of nanocomposites, percolation effect is of great importance. This effect is typically observed in polymer matrix reinforced with highly conductive inclusions (for example Carbon NanoTube (CNT)). When two inclusions are closer than a critical distance (tunneling distance), electrons can "jump" from one inclusion to another through the polymer matrix. This effect has a great influence on the electrical conductivity of the composite when the volume fraction of filler is greater than a threshold, called the percolation threshold (illustrated in figure 6). When the volume fraction reaches this threshold, a continuous path is formed and the composite becomes electrically conductive. Typical applications for this effect include composites with good antistatic or electromagnetic shielding properties.

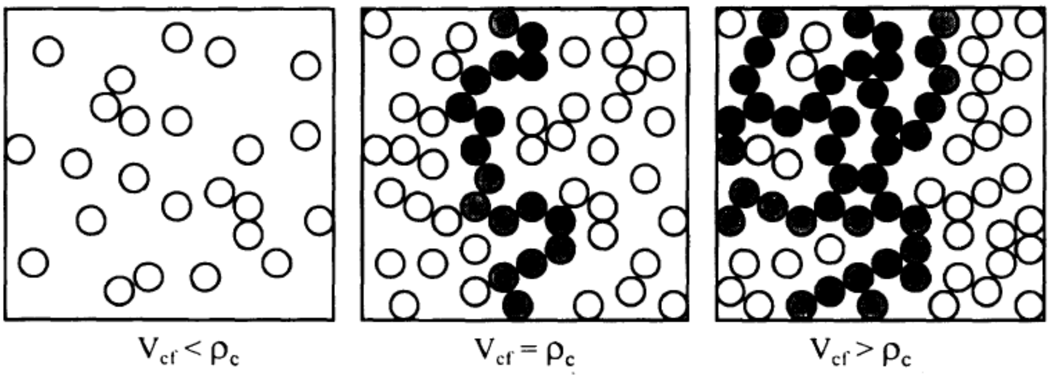


Figure 6: Illustration of the percolation threshold. When the volume fraction of filler is smaller than the percolation threshold, inclusions are well separated (left figure). When volume fraction reaches the percolation threshold, a continuous path of contacting inclusions is formed (center figure). Above the percolation threshold, multiple continuous paths exist. (Taken from [Olivero] Journal of Reinforced Plastics and Composites, Vol. 17, No. 8 (1998) p. 674-690).

A percolation model has been developed in Digimat-MF to be able to accurately simulate this effect. Figure 7 illustrates this model in the case of a PE matrix reinforced with carbon inclusion. The composite conductivity increases by several orders of magnitude when the volume fraction of inclusions reaches the percolation threshold.

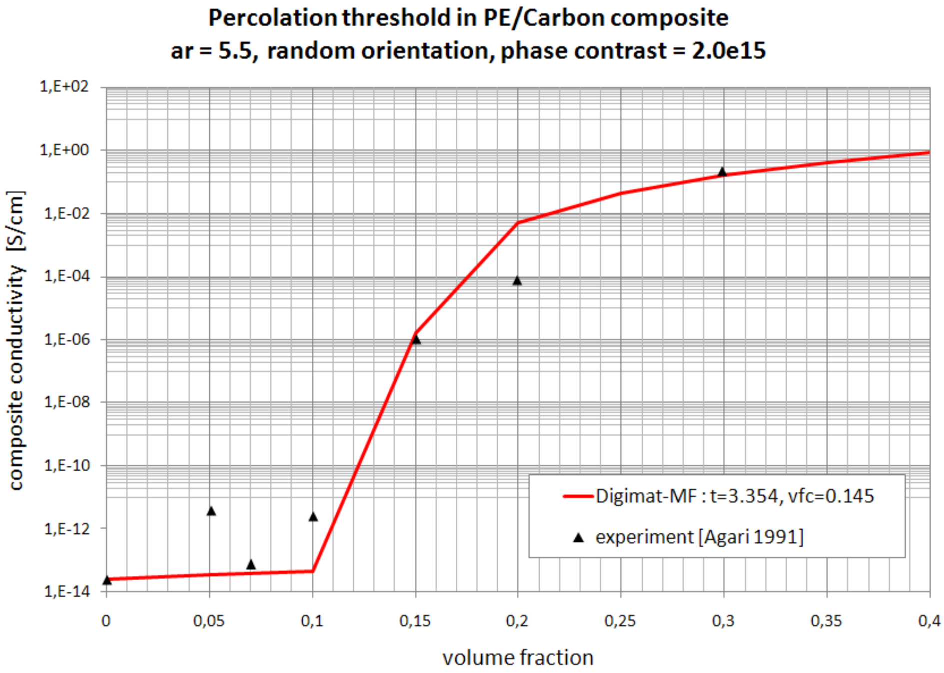


Figure 7: Illustration of the percolation model developed in Digimat-MF, and comparison to experimental data.

In conclusion, Digimat-MF offers an array of functionalities which are pertinent to nano-composite modeling: the ability to specify coatings (real or representative of one or more nano-effects), the ability to specify absolute coating thickness to investigate size-effects, and the ability to apply Multi-Level homogenization (homogenize A with B, then AB with C, then ABC with D, etc) to represent the multi-scale microstructure.

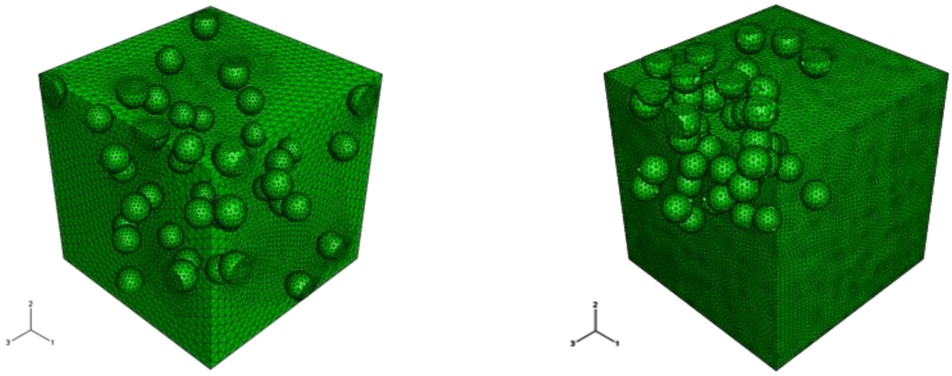
MODELING NANOCOMPOSITES WITH DIGIMAT-FE (FINITE ELEMENT MODEL OF MICROSTRUCTURE)

Digimat-FE is a micromechanical material modeling software that uses a direct, realistic finite element (FE) representation of a representative volume element (RVE) of the composite microstructure. Digimat-FE is complementary and fully interoperable with Digimat-MF. The main advantages of Digimat-FE with respect to Digimat-MF are:

1. The possibility to generate very complex RVE with ellipsoidal and/or non-ellipsoidal inclusions (e.g. semi-crystalline microstructure morphology);
2. Take into account geometrical effects such as inclusion clustering and percolation;
3. Compute the actual distribution of the local fields at the micro scale (i.e. in each phase of the composite) in addition to the macroscopic response of the composite.

However, the CPU time needed to set up and run a Digimat-FE model is much larger than for an equivalent Digimat-MF analysis, while the macroscopic response predictions of both approaches are comparable. Digimat-MF should thus be used for the initial analyses, while Digimat-FE can be used for verification and fine-tuning or for some situations where the assumptions behind Digimat-MF would be too restrictive.

Digimat-FE is used to generate very realistic RVE microstructure geometries, which can be exported in *step* or *iges* formats. Digimat-FE is interfaced with Abaqus/CAE for the semi-automatic meshing of the RVE microstructure geometry as well as the definition of materials, load and boundary conditions. Figure 8 shows an FE mesh of a polymer matrix filled with coated, spherical inclusions with and without clustering. Abaqus/Standard is then used to solve the nonlinear FE model. The final results can be post-processed as a regular Abaqus FEA solution, or within Digimat-FE to obtain micromechanical results such as the probability to reach a given stress, strain or failure indicator, for a given phase or for the composite. Figure 9 shows a RVE of a polymer matrix reinforced with carbon nanotubes. For this kind of composite, it has been shown that the carbon nanotubes are never perfectly straight, but rather wavy. This waviness has a very important influence on the mechanical properties of the composite, this is why the waviness of the carbon nanotubes is explicitly modeled here.



(a) (b)

Figure 8: **Semi-automatic meshing** of a polymer matrix reinforced with nano-filler that is (a) randomly distributed, or (b) clustered.

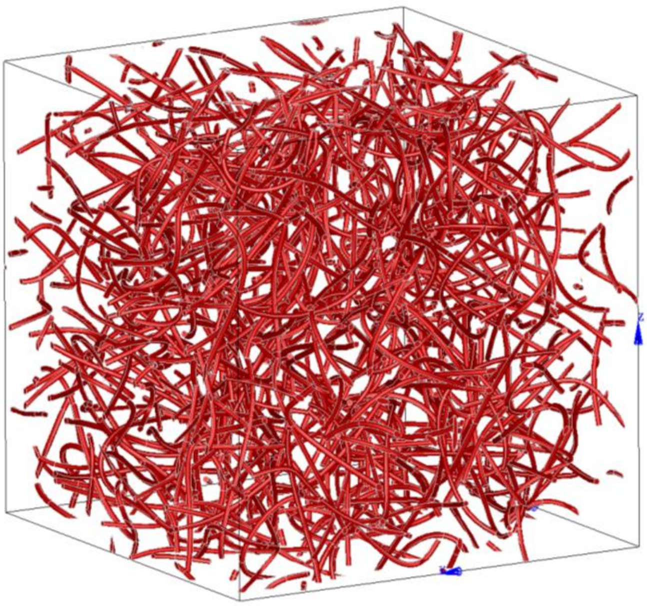


Figure 9: **RVE** of a polymer matrix reinforced with carbon nanotubes. The waviness of carbon nanotubes is explicitly modeled.

Here is what Digimat-FE has to offer with respect to nano-composite modeling:

- Clustering

  Digimat-FE offers a large number of options and parameters to design the microstructure of choice. One of the options is to enforce clustering of the inclusions. The user can specify the desired number of clusters, and the degree of clustering. For example, the user chooses to have 2 clusters in the RVE and then the generator randomly places inclusions so that there is a higher probability to find an inclusion close to one of the cluster centers (Figures 8 and 10).

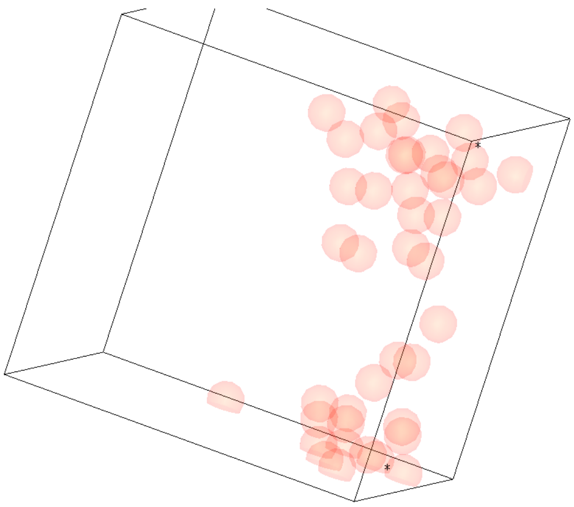


Figure 10: **Clustering**: RVE geometry with two cluster centers (indicated with *). Particles (red) are clearly grouped around the cluster centers.

- ## Size distribution of clusters

Figure 11 shows the geometry of an RVE with spherical inclusions of various sizes (size ratio 1:30). The size distribution can be specified in the phase pane in Digimat-FE: an inclusion size can be either constant, or random between a minimum and maximum value, or determined by a user defined size distribution (histogram).

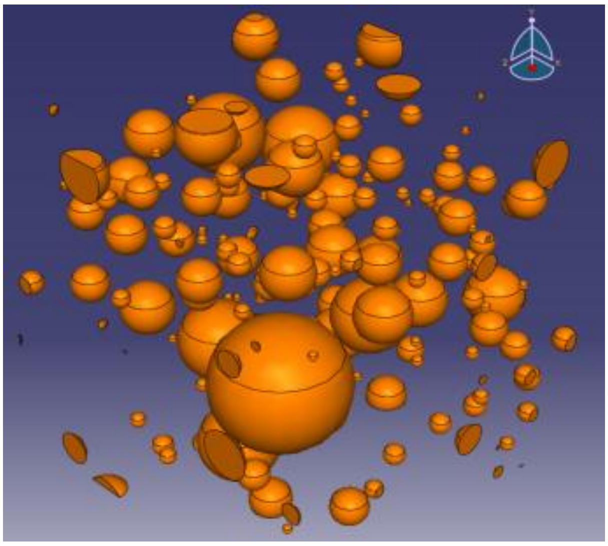


Figure 11: RVE geometry for a nano-filled polycarbonate with **size distribution** of nano-particle clusters.

- ## Particle-matrix interface and particle-particle interaction

The materials and microstructure definition of Digimat-MF is directly translated into Digimat-FE where it is ready to be used by the RVE geometry generator. In other words, any real or representative coatings, effective particle properties or effective cluster materials are transferred automatically from Digimat-MF to Digimat-FE. In case of coating, the RVE geometry generator will produce a microstructure geometry including the coating (if any) and obeying the mass or volume fraction of the phases as closely as possible. Moreover, Digimat-FE is able to generate geometries where the inclusions or the coatings intersect to a specified degree. This allows for enhanced modeling of interfaces and interactions.

In conclusion, Digimat-FE supports and continues the functionality of Digimat-MF, also for nanocomposite modeling. The two modules Digimat-MF and Digimat-FE are a complementary set of tools for the analysis of any composite material.

CASE STUDY 1: POLYCARBONATE MATRIX WITH MINERAL NANO-FILLER (COURTESY OF SOLVAY S.A.)

Let's consider the example of a polycarbonate (PC) matrix filled with mineral barite ($BaSO_4$) nano-particles. The average size of the nano-particles is less than 50nm. Two composites are considered: PC with 6% mass fraction barite, and PC with 15% mass fraction. The composite modulus was determined experimentally, see Table 1.

Analysis with Digimat-MF

Table 1 (second column) shows the experimentally determined values of the moduli of the two composites. These values can be compared to the values predicted by Digimat-MF without taking any nano-effects into account (third column), i.e. considering the composite to be a regular composite with micro reinforcements. In this case the Digimat-MF values are less than 14% off. In a second step the analysis was performed including two nano-effects described above:

- The clustering of the spherical barite particles into a dense packing with only voids in between.
- The barite particle-particle interaction, where it was assumed that, over a certain distance, the inter-particle forces are of the same order of magnitude as the intra-particle forces. As mentioned above, this interaction can be modeled using the coating functionality of Digimat-MF, see Figure 12.

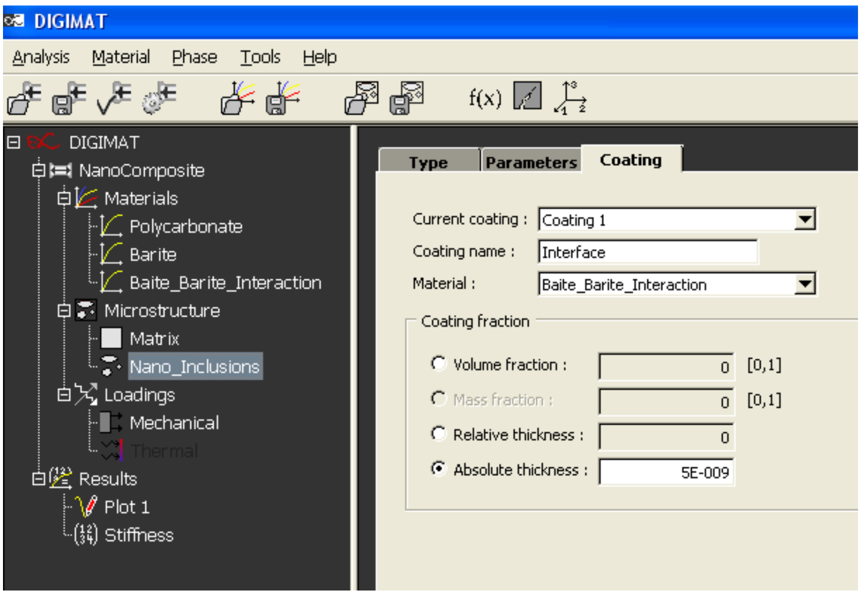


Figure 12: Digimat-MF graphical user interface uses a tree structure (on the left) to group the definition of Materials, Microstructure and Loading. The pane on the right offers various options to define an inclusion's **coating**, in this example a coating of 5 nanometer absolute thickness that represents the barite particle-particle interaction.

The predicted values are presented in the right-most column, and are even closer to reality due to the incorporation of two nano-effects into the model.

Composite modulus	experiment	Digimat-MF	Digimat-MF + nano-effects
PC + 6% $BaSO_4$	2480 MPa	2269 MPa (-9%)	2415 MPa (-3%)
PC + 15% $BaSO_4$	2729 MPa	2398 MPa (-14%)	2793 MPa (+2%)

Table 1: Comparison of composite modulus obtained from experiment and from Digimat-MF, with or without nano-effect modeling.

Analysis with Digimat-FE

An image analysis was performed using electron microscope images of varying magnification (up to 1nm, see Figure 3) of the nano-composite microstructure. The image analysis provides a histogram size distribution of the barite particle clusters. This size distribution can be used as input by Digimat-FE and is thus taken into account while constructing the RVE geometry, shown in Figure 10. The size distribution of the clusters is clearly visible. This complex RVE geometry is meshed (see Figure 13) and solved with Abaqus/Standard. The solution is then post-processed to find the composite modulus. The values obtained from the Digimat-FE are within 5% of the Digimat-MF values.

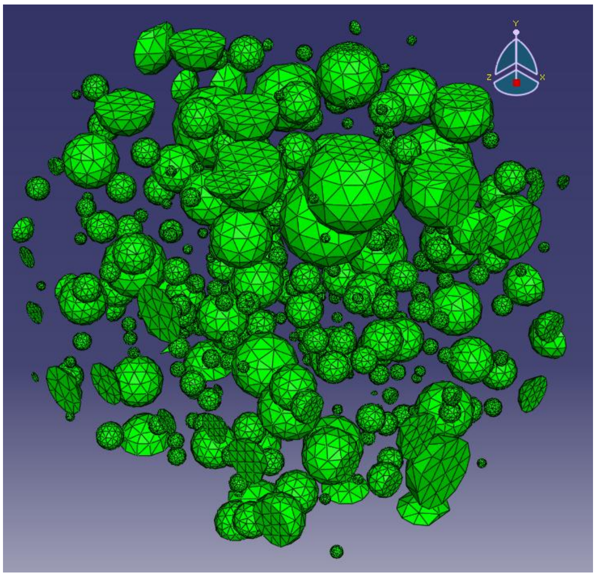


Figure 13: RVE mesh for a nano-filled polycarbonate with **size distribution** of nano-particle clusters.

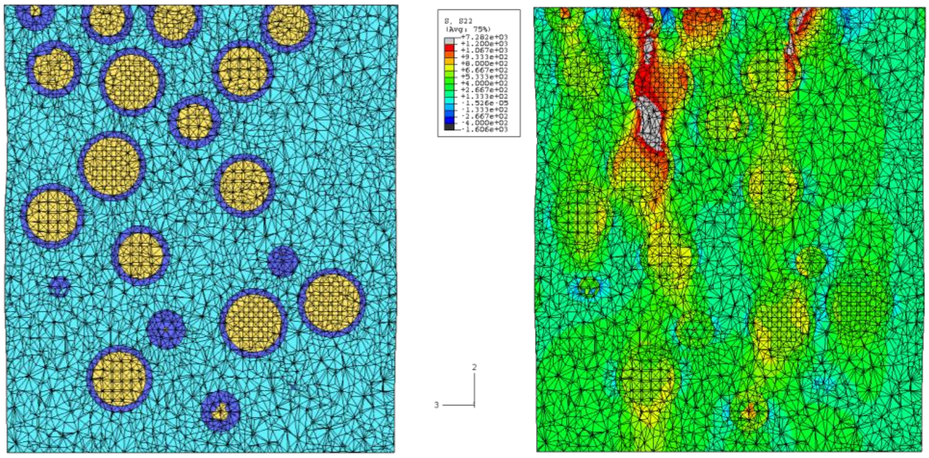


Figure 14: **Post-processing** of Digimat –FE to Abaqus solution. *Left:* cross-section of the mesh showing inclusions (yellow) with coating (purple). *Right:* stress distribution in the same cross-section; stress concentrations (red) occur where particles align in the direction of traction.

CASE STUDY 2: KERIMID MATRIX WITH AL_2O_3 INCLUSIONS

Digimat-MF and Digimat-FE can also be used to predict the thermal and electrical conductivities of a nanocomposite.

Let's consider the example of a Kerimid matrix reinforced with Al_2O_3 short fibers (aspect ratio = 6), with a random 2D orientations. Several samples were manufactured with different volume fractions of filler. The thermal conductivity of the composite was measured and compared to the predictions of Digimat-MF.

Analysis with Digimat-MF

The results are presented in Figure 14. Experimental data are taken from [Dunn], Journal of Composite Materials, vol 27, No. 15/1993.

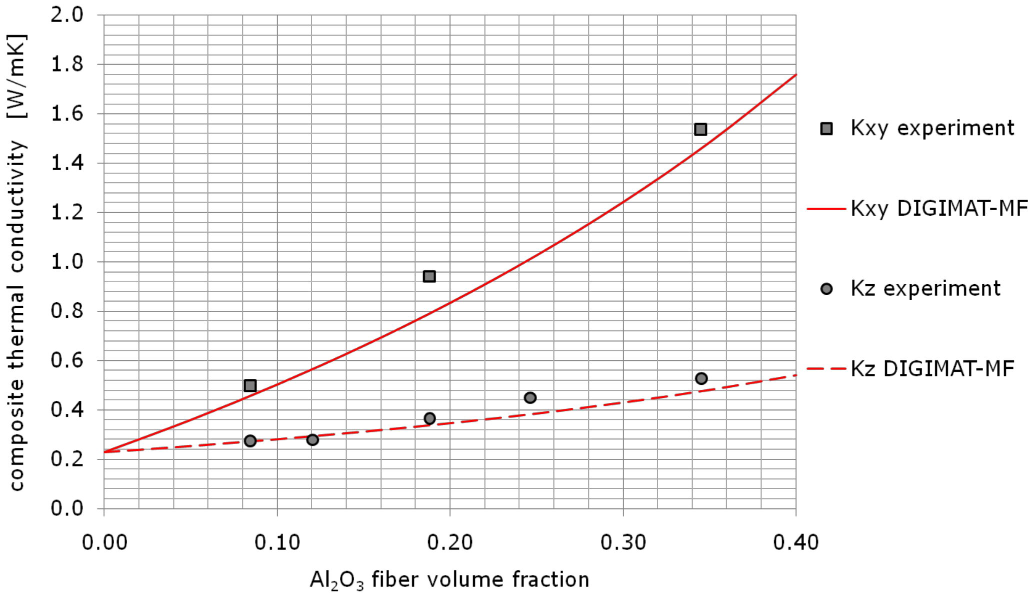


Figure 15: Comparison of the Digimat-MF predictions of the composite thermal conductivity to the available experimental values. Experimental data are taken from [Dunn], Journal of Composite Materials, vol 27, No. 15/1993.

Analysis with Digimat-FE

The same kind of analysis can be performed using Digimat-FE. A detailed finite element model (RVE) is built automatically, based on the statistical description of the material microstructure. This RVE is then submitted to a thermal loading using periodic boundary conditions. The figure 16 shows a contour plot of the first component of the heat flux vector. It was obtained with a prescribed temperature gradient in the 1-direction.

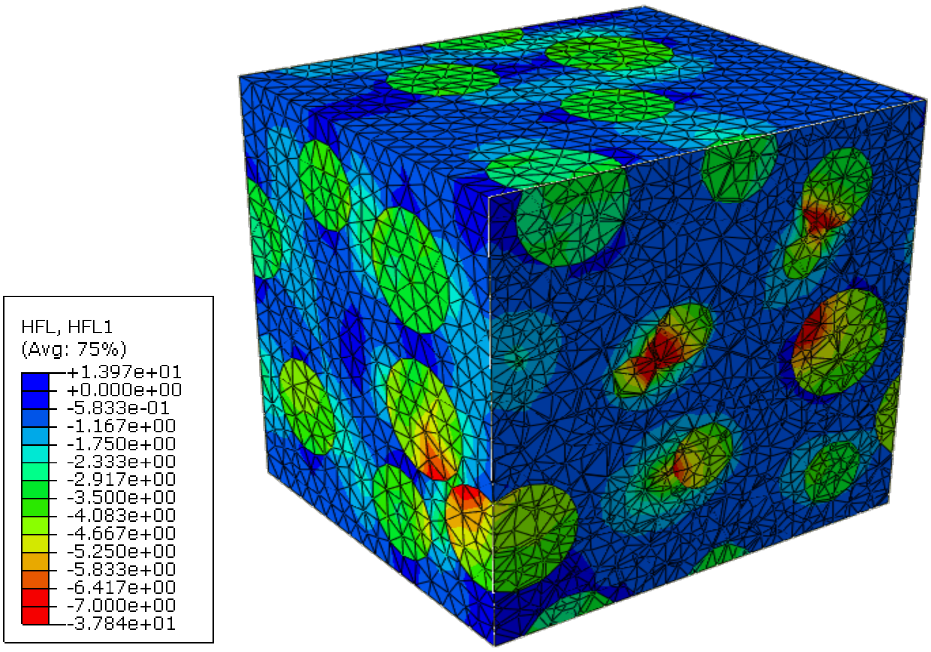


Figure 16: Heat flux resulting from a temperature gradient (1 K/m) in the 1-direction (units are K, m and W)

REFERENCES

[1] DIGIMAT, The Nonlinear Multi-Scale material & structure modeling platform

[2] DIGIMAT User Documentation, © e-Xstream engineering, 2009

[3] ABAQUS User Manual, © Dassault Systèmes, 2008

[4] Multi-Scale Modeling of Polymer Nanocomposites, L. Adam, K. Delaere, M. Kaszacs, J.-S. Gérard, R. Assaker and I. Doghri, NSTI Nanotech 2009 proceedings

[5] Prediction of the elastic properties of single walled carbon nanotube reinforced polymers: A comparative study of several micromechanical models, A. Selmi, C. Friebel, I. Doghri, H. Hassisl. Composites Science and Technology 67 (2007) 2071–2084

ACKNOWLEDGEMENT

The nano-composites modeling capabilities of DIGIMAT were partly developed in collaboration with Solvay S.A. We thank Mr. Dehennau, Mr. Blairon and Mrs. Kaszacs for giving us the opportunity to work on this subject and to validate our developments.

e-Xstream would also like to acknowledge the support of the Walloon Government support in the frame of the NanoCompo project

