Verifying Molecular Model of Montmorillonite Nanocomposites

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Summary. The density functional simulations (DFT) have been used to calculate elastic properties of montmorillonite clay platelets. A fully populated stiffness tensor has been calculated and all orthotropic elastic constants, for a first time, have been derived. The same model system and simulation parameters were used to predict Raman spectra which favorably compare with experimental data. The interfacial properties have been determined running molecular dynamics simulations with the force field which correctly predicts platelets spacing and infrared spectra of clay platelets.

1 INTRODUCTION

Any homogenisation technique attempting to predict overall material behaviour must contain properties and morphology of all elements composing material´s microstructure. In nanocomposite materials elementary building blocks include nano-reinforcing particles and their interfacial region with a surrounding matrix. In most instances, a direct measurement of mechanical properties of nanoinclusions and interfacial regions is beyond experimental accessibility. Then one turns to molecular dynamics or ab initio simulations to provide necessary parameters.

Adapting a set of calculations to simulate a given physical property involves construction of a model system and detailed manipulation of many options that are available in different simulation codes. However, with so many tuneable parameters and options, each potentially having a significant effect on the final result, the calculated property value possesses a large uncertainty margin. This drawback can be significantly reduced calculating, with the same model and set of parameters, another parent property that is experimentally verifiable.

2 ANALYSIS

A unit cell of montmorillonite platelet has been optimized using density functional theory (DFT) that incorporates electronic structure of the system into calculations. Optimized structure of the platelet has been used for a subsequent calculation of elastic constants. Elastic constants are calculated from stress-strain diagrams obtained from six loading configurations: three tensile deformations and three shear deformations each performed stepwise with minimization calculations performed after applied loading step. A full population of stiffness constants and corresponding compliance constants is obtained from which orthotropic engineering constants have been extracted. Since the determination of montmorillonite elastic constants is not experimentally accessible, the same model system and simulation parameters

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were used to predict Raman spectra which favorably compare with experimental data as shown in Fig. 1, thus indirectly confirming reliability of the elastic constants´ calculation.

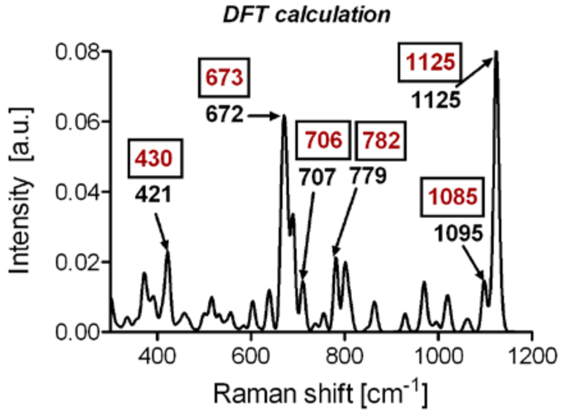

Fig. 1. Raman spectrum from DFT calculation and experimentally detected Raman peaks (in boxes).

A similar strategy has been used to predict interfacial properties in clay/polypropylene nanocomposites by using molecular dynamics simulations. The influence of different organo-modifying species on the interfacial bonding and their impact on the constrained region surrounding the clay has been determined running molecular dynamic simulations with appropriately selected force field. Verification of the interphace model and force field parameters has been made by calculating infrared spectra and clay platelets distances in the gallery. Both quantities resemble very closely experimental results from X-ray diffraction and spectroscopic measurements.

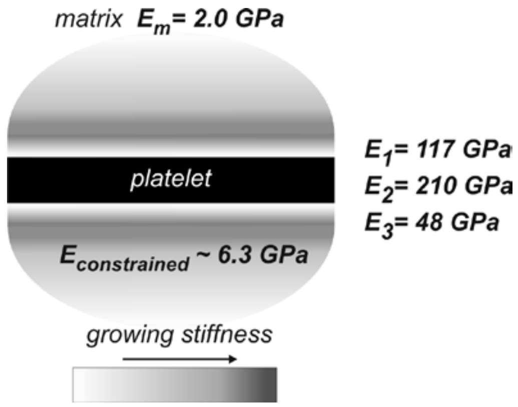

Fig. 2. The clay platelet and its interphase.

Figure 2 symbolically illustrates the interphase region and corresponding mechanical quantities. The platelet is surrounded by a constrained region with limited chain mobility and its averaged stiffness that is significantly larger than the pristine matrix stiffness. The constrained region may extend to several tens volume fraction percent depending on the loading concentration of clay platelets dispersed in the matrix.