Multiscale Molecular Modeling of Hybrid Organic-Inorganic Nanocomposites of Type I and II

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Abstract. A current challenge of physical, chemical and engineering sciences is to develop theoretical tools for predicting structure and physical properties of hybrid organic inorganic nanocomposite from the knowledge of a few input parameters. However, despite all efforts, progress in the prediction of macroscopic physical properties from structure has been slow. Major difficulties relate to the fact that (a) the microstructural elements in multiphase material are not shaped or oriented as in the idealizations of computer simulations, and more than one type can coexist; (b) multiple length and time scales are generally involved and must be taken into account, when overall thermodynamic and mechanical properties wish to be determined, and finally (c) the effect of the interphases/interfaces on the physical properties is often not well understood and characterized. As a consequence, their role is often neglected in the development of new theoretical tools or they are treated in a very empirical way. In this work, we focused on issues (b) and (c) in a multiscale molecular simulation framework, with the ultimate goal of developing a computationally-based nanocomposite designing tool. In particular, we developed a hierarchical procedure in which lower scale (i.e., QM, MD and /or MC) simulations are performed to obtain parameters for higher scale (i.e., mesoscopic and/or finite element) calculations, from which the bulk properties of the hybrid nanocomposite material can be ultimately estimated.

Introduction

Nanotechnology is one of the key technologies of the 21st century. The unique properties of nanostructured materials have now been elucidated for several years. A wet chemical method creating nanocrystalline or nanoscaled amorphous materials is the sol-gel process [1]. With this well-established synthesis technique inorganic materials (glassy or ceramic) and hybrid inorganic-organic (I/O) polymers or nanocomposites can be processed to form (nano)particles, coatings, fibers, or bulk materials. Inorganic sol-gel-derived materials had been investigated and commercialized a few decades ago and, due to the profound understanding of the underlying chemical and technical processes, are still present as important examples of large-scale applications of the sol-gel technology [2].

To a certain extent, these hybrid materials combine the most important properties of their constituents, like high transparency (glass-like), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), and are easily accessible because of an unique availability of the respective precursors (commercially available metal alkoxides and organo(alkoxy)silanes as well as nanoparticles). Besides the simple metal or silicon alkoxides that - after hydrolysis - lead to the formation of an inorganic oxidic network, organo(alkoxy)silanes can be used to incorporate

polymerizable organic substituents (epoxy, vinyl, or methacryloxy groups) into the final product, because the Si-C bonds in these molecules are stable under the mild conditions of sol-gel processing. The polymerization reactions of the functional organic groups can be induced by thermal or photochemical means, thereby cross-linking the preformed nanosized inorganic moieties.

Inorganic-organic hybrids can be grossly divided into two major classes [3]. In *class I*, organic molecules, pre polymers or even polymers are embedded in an inorganic matrix. These materials are synthesized by carrying out the hydrolysis and condensation of the inorganic compound, i.e., the formation of the inorganic network, in the presence of the organic compound or by polymerizing organic monomers in porous inorganic hosts. Only weak bonds exist between both phases. In *class II*, the inorganic and organic components are connected by covalent bonds. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol-gel processing and the organic moieties.

If the hybrid system is not built up from nanocrystalline components, the intricate mixture of inorganic and organic phases in most cases leads to amorphous materials. Further, Because of the complexity of the possible chemical reactions and the numerous parameters influencing the hydrolysis and condensation of organo-(alkoxy)silanes (pH, temperature, catalyst, water/silane ratio) a more or less broad distribution of dimers, oligomers, and higher condensation products can be expected. The results can be interpreted in the sense of initial formation of small clusters or oligomers, which grow to larger polycondensates presumably by a cluster-cluster aggregation mechanism. The peripheral positions of the organic substituents are important to allow subsequent polymerization reactions to cross-link the individual inorganic condensates and embedding them into an organic matrix. The high transparency of the resulting hybrid polymers is a further hint to their submicrometer or nanostructural phase size. Thus, hybrid polymers can be regarded as nanocomposites with a *transparent filler*.

3-glycidyloxypropyltrimethoxysilane (GPTMS) is an organofunctional alkoxysilane monomer that can undergo both the sol-gel polymerization of the alkoxy groups and curing of the epoxy functionality to form an I/O hybrid network with covalent bonds between organic and inorganic phases. Routinely, polymerization of GPTMS is carried out by a sol-gel process which leads to the formation of I/O hybrid structures with pendant, unreacted epoxy functionalities that are prone to later, eventual curing [4]. To obtain optimized formulations and efficient technological processes, however, extensive experimental campaigns must be carried out; further, some sound theories in conjunction to experiments must be developed, in order to gain some fundamental knowledge about the physical/chemical phenomena at the basis of the properties of these materials. In this work we present a computational strategy to obtain realistic molecular models of crosslinked polymer networks based on a molecular dynamics (MD) Perl script for the *Materials Studio* software platform. This methodology has been applied to mimic the formation of 3D hybrid I/O networks based on the condensation reaction of GPTMS under acid conditions. Further MD simulations were then carried out to predict some material properties of the network structures thus obtained.

Computational details

General computational procedure. A fully hydrolyzed GPTMS molecule was selected as starting monomer, and its condensation reaction under acid conditions was considered. This practically corresponds to a situation in which only the creation of Si-O-Si bonds between the available Si-O-H moieties takes place, leaving the epoxy groups unreacted [5]. For the generation of the final crosslinked system, we adopted the following general scheme. Briefly, the molecular model of the hydrolyzed GPTMS molecule was built and its geometry optimized using the COMPASS forcefield (ff) [6] (Step 1). 100 hydrolyzed GPTMS molecules were then packed into a simulation box under periodic boundary conditions. 100 different simulation boxes were independently created and, after geometry relaxation of each 3D box, the one with the lowest energy value was selected (Step 2). The selected 3D box containing the initial GPTMS monomer system was subjected to geometry optimization followed by simulated annealing (8 cycles of 1000 MD steps , temperature range 200K - 500K). 5000 steps of molecular dynamics (MD) at room temperature (298 K) were then carried

out. All simulations were conducted in the canonical (NVT) ensemble, using an integration time step of 0.2 fs, giving a total annealing time of 1.6 ps, and an overall MD time of 1 ps (Step 3). Finally, the distances between the reactive atoms (O and H atoms from each OH group linked to the Si atom of GPTMS) were measured, the three closest pairs of reactive atoms whose distances were smaller than the selected reactive cutoff distance (3 Å) identified, and between the corresponding Si atoms new Si-O-Si bonds were created. Accordingly, an equivalent number of water molecules were deleted from the system (see Figure 1).
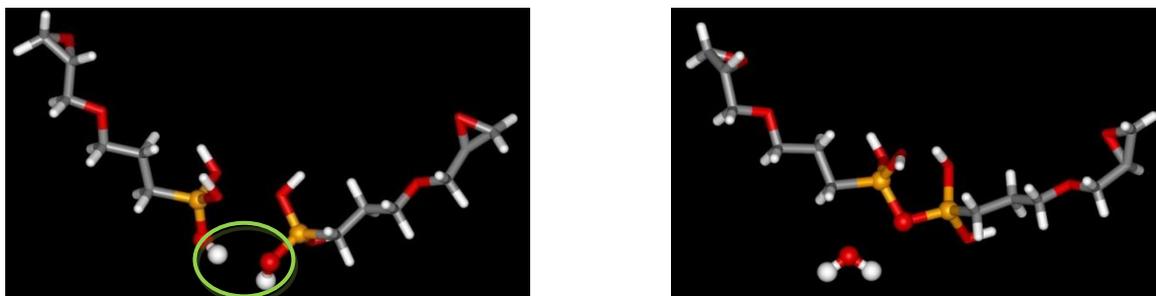

Figure 1. Details of the GPTMS molecular modeling showing (left) the reactive atoms and (right) the newly formed Si-O-Si bond with the corresponding deleted water molecule. All atoms are in stick rendering, except for the atoms involved in new bond formation, which are portrayed in stick-and-ball. Color code: Si, gold; O, red; C, gray, H, white.

The reactive cutoff distance was increased during the networking formation from 3 Å to 6 Å. Since the presence of small, strained rings (i.e., with less than 4 Si atoms) in the final system is not found experimentally in hybrid I/O systems based on GPTMS, the necessary restrictions were implemented in the corresponding script, as described in details in the following paragraph. (Step 4). Steps 3 (referred to the actual cell) and 4 were repeated until no more pairs of reactive atoms satisfying all criteria were detected in the system. The whole network formation procedure was achieved by writing a Perl script using the object library available in *Materials Studio* (v. 4.1, Accelrys Inc. San Diego, USA).

3D network thermophysical properties determination. The 3D network structure obtained with the procedure described above was relaxed by performing annealing cycles up to 600K. The minimum energy structure was selected for further NVT and NPT molecular dynamics simulation at 300K for data collection. In particular, a constant strain minimization method was applied to the equilibrated 3D I/O network system to obtain the system stiffness matrix and, hence, the mechanical moduli via the Lamé constants. Finally, specific heat capacity at constant pressure C_P, was obtained from the fluctuations of energy in the isothermal-isobaric ensemble (NPT).

Results and discussion

The application of the procedure outlined above led to the successful generation of an hybrid I/O 3D system based on GPTMS with high conversion. It is well known that a 100% conversion is rarely achieved experimentally because of gel transition and glass transition at later stage. Although other systems with a different (lower) conversion degree α could be generated by changing, for instance, the distance between close contacts up to a reasonable value of 10 Å, the amount of unreacted group in the actual simulated molecular systems is, on average, equal to 10%, yielding $\alpha = 0.9$.

The central unit cells of the initial GPTMS monomers, and the final network systems obtained from the simulation are shown in Figure 2. As can be seen this Figure, the 3D network structures is characterized by the presence of both chemical crosslinks and physical entanglements. Some bonds clearly connect to image cells across the boundary, and thus extend throughout the periodic system. Due to the scarcity of experimental characterization, which by the way accounts for the small number of simulation studies on crosslinked polymeric systems, only a few comparisons between

experimental and simulation can be attempted based on the main structural features of the systems. Generally speaking, according to the polymerization conditions employed different structures for the resulting GPTMS networks are proposed, such as randomly connected three-dimensional networks of trifunctional monomers, "ladder" structures, and a combination of linear, "ladder" and cage-like fragments [7].
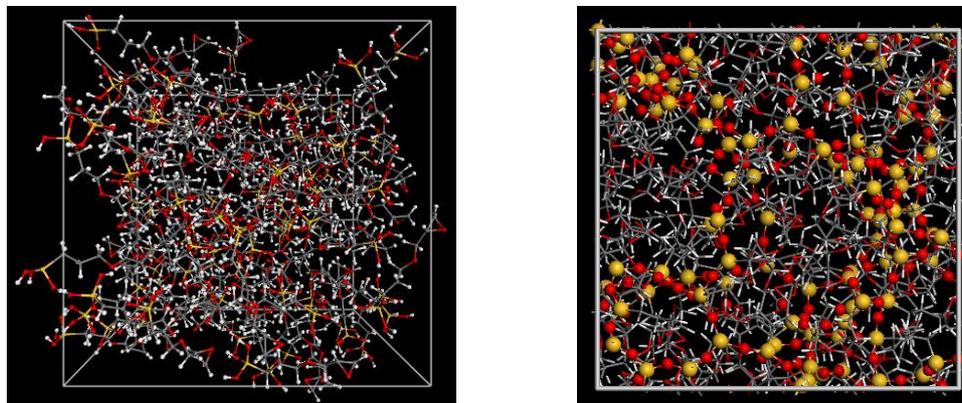

Figure 2. (left) Central unit cell of the initial GPTMS monomers. (right) Hybrid I/O 3D network structure obtained starting from the GPTMS simulation cell (left) and applying the Perl script developed in this work. Crosslinked Si and O atoms are highlighted in stick-and-ball. Color code as in Figure 1.

As the presence and relative amount of the structures described above significantly affect the network final structure, homogeneity and, ultimately, the mechanical properties of the resulting hybrids, the different reaction steps can be optimized to obtain final materials with targeted properties. Experimentally, it has been found that, under acid conditions, only a very small amount of cage-like structures are formed in the GPTMS polymerization, the intermolecular condensation being the preferred mechanism of network growth [5]. The corresponding composition of the gel state exhibits a considerable amount of silicon atoms involved in triple intermolecularly branched units representing the cross-links in the network; further, no microphase separation resulting in self-assembly of regularly arranged domains has been detected [5]. The inspection of the 3D structures obtained from our simulation procedure compare well with the network picture described above. Indeed, the overall network structure is linear and extends in all three directions, the presence of unstrained rings with a number of Si atoms greater being observed.

The mechanical properties and the constant pressure heat capacity calculated using the 3D network structures obtained from the MD simulations discussed above are reported in Table 1. The range of experimental values of the corresponding mechanical properties are reported in parenthesis (43,44) for comparison. As can be seen from this Table, all calculated properties of the GPTMS network lay in the expected range.

Property	Value
E (GPa)	3.74 (1.9 − 4.5)
B (GPa)	2.62 (2.5 − 7)
G (GPa)	1.48 (0.9 − 1.5
C_p (kJ/kgK)	1.57 (1.1 − 2.2)

Table 1. Young modulus E, bulk modulus B, shear modulus G, and constant pressure heat capacity Cp for the 3D GPTMS-based I/O network structures obtained from MD simulations.

Conclusions

In this work a computational procedure, based on a Perl script developed in Materials Studio v. 4.1, was developed, which allowed to obtain atomistic models of hybrid organic/inorganic networks

based on GPTMS. The actual procedure, however, could be applied with minor modifications to any similar system. The simulation allowed also to estimate several thermophysical properties of the 3D network, such as mechanical moduli and constant pressure specific heat, whose values were found to be in the range of the corresponding experimental evidence for similar systems. These results confirm both the accuracy of the 3D model structure generated by the script procedure, and the quality of the force field used. Therefore, the proposed computational recipe can constitute a useful tool for the design and development of new hybrid I/O systems with improved structural/chemico-physical properties.

Acknowledgements

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