Chapter 2
Modelling and Simulation of Sol-Gel Nanocomposites

Paola Posocco, Sabrina Pricl and Maurizio Fermeglia

Abstract Modelling and simulation of sol–gel nanocomposites is a promising method for understanding the properties at molecular level and consequently improving and quickening the design of such materials. In the present chapter, a hierarchical procedure for bridging the gap between atomistic and macroscopic modelling via mesoscopic simulations will be presented and discussed. Multiscale molecular modelling is first introduced as a general concept and then applied to sol–gel nanocomposites. The procedure is applied to a model system, chosen as typical of sol–gel nanocomposites, namely the 3-glycidoxypropyltrimethoxysilane (GPTMS) network with ZnS nanoparticles dispersed in the organic matrix. Details of each scale simulation protocols as well as the scales integration are given in this chapter. Finally, it is shown how macroscopic properties of the sol–gel nanocomposite of interest are estimated using the multiscale molecular simulation protocol described. Calculated values at different scales, but particularly at macroscale are compared with experimental data to show the reliability of the proposed approach.

2.1 Introduction

Sol–gel nanocomposites are functional organic–inorganic materials made by a matrix (organic, inorganic, or hybrid) and one (or more) dispersed solid (inorganic) phase [1]. Sol–gel synthesis normally gives rise to a type II interpenetrating network [2] nanostructure characterized by chemical bonds and by strong van der Waals antiparticle interactions, which are partly responsible for the nanostructure. Moreover, the effective interactions between nanofillers are also influenced by the polymer–particle interactions. Additionally, the nanoparticle (NP) geometry—such
as platelet or sheet-like particles, nanotubes, or polyhedral nanoparticles—possesses a large impact on property changes, since it can affect both surface energetics and surface-to-volume ratio [3–6]. To affect high-technology applications requiring unique electrical, thermal, and optical properties, manufacturing techniques enabling control of nanoparticle arrangement and distribution are mandatory. A precise morphology control is of paramount importance.

To this purpose, the development of theories and the application of computer simulation techniques have opened avenues for the design of these materials, and the a priori prediction/optimization of their structures and properties [7]. Polymers are complex macromolecules that display structure ranging from the Å level of the individual backbone bond of a single chain to the scale of the radius of gyration, which can reach tens of nanometres. Polymeric structures in melts, blends, and solutions can range from nanometre scales to microns, millimetres, and larger. The corresponding timescales of the dynamic processes relevant for different materials properties span an even wider range, from femtoseconds to milliseconds or even seconds or hours in glassy materials or for large-scale ordering processes such as phase separation in blends. No single model or simulation algorithm can span this range of length and timescales. Thus, one of the most important issues in computational materials research, which holds particular challenges for polymer materials, is multiscale simulation—the bridging of length and timescales and the linking of computational methods to predict macroscopic properties and behaviour from fundamental molecular processes. The idea of performing simulations of materials across several characteristic length and timescales starting from fundamental physical principles and experimental data has obvious appeal as a tool of potentially great effect on technological innovation and material design [8].

The aim of the present contribution is not a thorough review of the current multiscale molecular modelling techniques available in the literature (for which the reader can refer to [7, 9, 10]), but rather to present the authors’ view on the possibilities that multiscale modelling offers in the understanding and controlling the properties of nanocomposite materials obtained by the sol–gel method and tailoring them for specific applications. The examples presented in this overview reflect authors’ own research interests and are by no means exhaustive. Nevertheless, it is our hope that they can give a satisfactory cross section of the current state of the field and can serve as inspiration for further developments in this exciting branch of science.

2.2 Multiscale Molecular Modelling

Multiscale Molecular modelling and simulation combines methods that cover a range of time and length scales in order to study material systems. In the context of materials simulations, four characteristic time and length levels can be envisaged before reaching the last step that is the engineering design (Fig. 2.1):
1. the *quantum scale* ($\sim 10^{-10} \text{ m and } \sim 10^{-12} \text{ s}$), in which nuclei and electrons are the main players, and their quantum–mechanical state dictates the interactions among atoms. The possibility of obtaining data describing structural and electron features of the system being considered and the possibility of taking into account effects associated with the break and formation of chemical bonds in molecules, changes in electron configurations, and other similar phenomena are the main advantage of methods working at quantum scale;

2. the *atomistic scale* ($\sim 10^{-9} \text{ m and } 10^{-9} - 10^{-6} \text{ s}$). In atomistic simulations, all atoms are explicitly represented, or in some cases, small groups of atoms are treated by single sites referred to as pseudo atoms. The potential energy in the system is estimated using a number of different classes of interactions, typically (i) bonded interactions, including bond-length (stretch) potentials, bond-angle (bend) potentials, torsion (twist) potentials, and cross-terms and (ii) non-bonded interactions, which in general consist in Coulomb interactions and dispersion forces;

3. the *mesoscopic scale* ($\sim 10^{-6} \text{ m and } 10^{-6} - 10^{-3} \text{ s}$). In these methods, a molecule is usually treated with a field description or microscopic particles that incorporate molecular details implicitly. Therefore, they are able to simulate phenomena on length and timescales currently inaccessible by classical atomistic approach;

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**Fig. 2.1** The diagram illustrates the concept of a unified message-passing, sequential multiscale approach able to reach length and timescales that individual methods fail to achieve. At the same time, this unified approach retains the accuracy that the individual techniques provide in their respective scales. The main objective of multiscale approaches is to predict the performance and behaviour of materials across all relevant length and timescales, striving to achieve a balance among accuracy, efficiency, and realistic description.
4. the macroscopic scale \((\sim 10^{-3} \text{ m and 1 s})\), where a constitutive law governs the behaviour of the physical system, which is considered as a continuous medium, ignoring discrete atomic and molecular structures and their influence on overall system behaviour. The final aim consists in representing a heterogeneous material as an equivalent homogeneous one.

At each length and timescale, well-established and efficient computational approaches have been developed over the years to handle the relevant phenomena. To treat electrons explicitly and accurately at the lower scale, methods classified as quantum mechanics (QM) can be employed. QM methods have undergone enormous advances in the past 10 years, enabling simulation of systems containing several hundred atoms with good accuracy [11, 12]. For material properties at the atomic level, molecular dynamics (MD) and Monte Carlo (MC) simulations are usually performed employing classical interatomic potential, which can often be derived from QM calculations [13, 14]. Although not as accurate as QM methods, the classical simulations MD and MC are able to provide insight into atomic processes involving considerably larger systems [15–17]. At the mesoscopic scale, the atomic degrees of freedom are not explicitly treated, and only larger-scale entities are modelled, that is agglomeration of atoms, called bead, obtained through a coarse-graining procedure. Mesoscale techniques are particularly useful for studying the behaviour of polymers and soft materials. They can model even larger molecular systems, but with the commensurate trade-off in accuracy [18–20]. Typical results of mesoscale simulation are the morphology and the structure of the matter at nanoscale level at the desired conditions of temperature, composition, and shear. Various simulation methods have been proposed to study the mesoscale structures in polymer-based materials, the most common being Brownian dynamics (BD) [21–23], dissipative particle dynamics (DPD) [24–26], lattice Boltzmann (LB) [27], time-dependent Ginzburg–Landau (TDGL) theory [28], and dynamic density functional theory (DDFT) [29–32]. Eventually, it is possible to transfer the simulated mesoscopic structure to finite-elements modelling (FEM) tools [33, 34] to calculate macroscopic properties for the systems of interest (Fig. 2.2).

The ultimate goal of a multiscale modelling is hence to predict the macroscopic behaviour of an engineering process from first principles, i.e. starting from the quantum scale and passing information into molecular scales and eventually to process scales. One computes information at a smaller (finer) scale and passes it to a model at a larger (coarser) scale by leaving out (i.e. coarse graining) degrees of freedom [35–37]. Two ingredients are required to construct a successful sequential multiscale model: first, it is necessary to have a priori and complete knowledge of the fundamental processes involved at the lowest scale. This knowledge or information can then be employed for modelling the system at successively coarser level. Second, it is necessary to acquire a reliable strategy for encompassing the lower-scale information into the coarser scales. This is often accomplished by phenomenological theories, which contain a few key parameters, the value of which is determined from the information at the lower scale. This message-passing
approach can be performed in sequence for multiple-length scales. The key attribute of the sequential approach is that the simulation at a higher level critically depends on the completeness and the correctness of the information gathered at the lower level, as well as the efficiency and reliability of the model at the coarser level. To obtain first-principles-based results for macroscale systems, we must ensure that each scale of simulation overlaps sufficiently with the finer description so that all input parameters and constitutive laws at each level of theory can be determined from more fundamental theory. Equally important we must ensure that these relations are invertible so that the results of coarse-level simulations can be used to suggest the best choices for finer-level parameters, which can be used to suggest new choices of composition and structure. The problem for polymers is that the method of coarsening the description from atomistic to mesoscale or mesoscale to continuum is not as obvious as it is going from electrons to atoms [38]. In other words, the coarsening from QM to MD relies on basic principles and can be easily generalized in a method and in a procedure, while the coarsening at higher scales is system specific. In this respect, for example, Doi [36] developed a suite of simulation tools that model polymers at the molecular and mesoscale level. Although each tool performs calculations using only one technique, the output from one level can be used directly as input for another, allowing an off-line bridging of length and timescales. To achieve what he and others refer to as “seamless zooming”, namely the ability to spawn higher-resolution simulations
using more detailed methods where needed, will require additional theoretical and computational advances. Along similar lines, off-line multiscale simulations of nanofilled polymers using coarse-grained molecular dynamics, mesoscopic time-dependent Ginsburg–Landau theory, and macroscopic continuum finite-element techniques have been carried out. Significant advances in uniquely mapping atomistic models of polymers onto coarse-grained models [39–43] have been made in recent years, in some cases providing nearly exact quantitative agreement between the two models for certain quantities. Scale integration in specific contexts in the field of polymer modelling can be done in different ways. Any “recipe” for passing information from one scale to another (upper) scale is based on the definition of multiscale modelling which considers “objects” that are relevant at that particular scale, disregards all degrees of freedom of smaller scales, and summarizes those degrees of freedom by some representative parameters. All approaches are initially based on the application of a force field that transfers information from quantum chemistry to atomistic simulation. From atomistic simulation to mesoscale model, essential features of the system have to be maintained while reducing the degree of freedom. So far, the features chosen for the reproduction by coarse-grained models have been mainly structural, thermodynamical, or both, with structure prevailing [39]. This linking through the mesoscale in which we can describe microstructure is probably the most challenging step towards the developing reliable first-principles methods for practical material’s design applications.

To accomplish these challenging goals, we illustrate here a computational strategy to obtain realistic molecular models of crosslinked polymer network-based nanocomposites. We consider a model system based on a 3-glycidyloxypropyltrimethoxysilane (GPTMS) network; “pre-made” nanoscale building blocks, i.e. ZnS nanoparticles, are dispersed in the sol–gel-derived hybrid system. This is intended to mimic the so-called ex situ sol–gel route, one of the more suitable-to-synthesis methods for large-scale industrial applications. The nanoparticles are chemically modified with (3-mercaptopropyl)trimethoxysilane (MPTMS), in order to evaluate the influence of the surface engineering on the interface energies between nanoparticles and matrix and ultimately on their aggregation behaviour. Briefly, our procedure consists in the following: (a) development of a molecular dynamics (MD) procedure to mimic the formation of 3D hybrid O/I networks based on the condensation reaction of GPTMS under acid conditions; (b) quantum/force field-based atomistic simulation to derive molecular interaction energies between GPTMS matrix and ZnS nanoparticle; (c) mapping these values onto mesoscopic dissipative particle dynamics (DPD) parameters; (d) mesoscopic simulations to determine system density distributions, nanoparticle dispersion, and morphologies; a reactive dissipative particle dynamics approach was employed to reproduce the reticulation of the polymer matrix at mesoscale level; and (e) simulations at finite-element level to calculate the relative macroscopic properties of the nanocomposite.

The example reported here should be considered a model system, and the same protocol may be applied to different system, adjusting the details.
2.3 Atomistic Simulation of GPTMS Crosslinked Matrix

Molecular dynamics (MD) is the method of choice for performing atomistic simulation [16]. In MD, the Newton atomic equations of motion are integrated numerically by the Verlet leapfrog algorithm. The atoms are moved by intermolecular potential, and a force field is defined in each position of the tridimensional box. Simulation is done by assuming a statistical mechanics ensemble of reference (NPT or NVT). Temperature is controlled via weak coupling to a temperature bath, pressure is kept constant by coupling to a pressure bath, and partial charges are updated regularly during the entire MD runs. Each MD run is started by assigning initial velocity for the atoms according to a Boltzmann distribution. After an equilibration phase (normally 50–100 ps), during which system equilibration is monitored by recording the instantaneous values of the total, potential, and kinetic energy and the time evolution of the volume, the data collection phase is started (normally up to 300–500 ps). With this procedure, MD is able to determine the thermodynamic properties at equilibrium for the molecular system at the desired thermodynamic conditions and to estimate interaction energies among components.

2.3.1 Model Building and General Computational Recipe

The general procedure for the generation of a hybrid O/I system based on GPTMS monomer starts by choosing the simplest conditions leading to the condensation network. Accordingly, a fully hydrolysed GPTMS molecule was modelled and its condensation reaction under acid conditions [44], i.e. only the creation of Si–O–Si bonds between the available Si–O–H moieties, was considered, leaving the epoxy groups unreacted (Fig. 2.3).

For the generation of the final crosslinked system, a detailed general computational recipe is applied. The procedure is fully described in the literature [45] and is based on a molecular simulation script that mimics the polycondensation reaction that takes place in the formation of the network. It is based on 5 consecutive steps. In the first step (1), COMPASS force field [46] is used to generate the molecular models of GPTMS monomers. Figure 2.4 shows the geometry-optimized molecular model of the GPTMS molecule, along with the atom labelling used in this work. For this monomer, the relevant structural parameters are listed in Table 2.1. In order to test the influence of the partial charge distribution on the physical properties of the final crosslinked system, we also assigned to the previously geometry-optimized
molecule a partial charge scheme obtained recharged using the quantum semi-empirical method AM1-ESP as implemented in the Vamp toolbox of Materials Studio version 5.5. At the end of step 1, then, two molecular models of the hydrolysed GPTMS monomer with the identical shape but different partial charges were obtained and used for further calculations. In the step 2, 100 hydrolysed GPTMS molecules were packed into a simulation box under periodic boundary conditions using the Amorphous Cell builder modulus of Materials Studio version 5.5 with initial density of the liquid mixture set to 1.57 g cm$^{-3}$ (assuming an ideal case of 100 % condensation). In the third step (3), the selected 3D boxes containing the initial GPTMS monomer systems were first subjected to a geometry optimization (2,000 steps), followed by a simulated annealing. The fourth step (4) is dedicated to the condensation reaction. The distances between the reactive atoms (O and H atoms from each OH group linked to the Si atom) were measured and ordered in an increasing order. The three closest pairs of reactive atoms whose distances were smaller than the selected reactive cut-off distance (3 Å) were identified, and between the corresponding Si atoms, new Si–O–Si bonds were created. An equivalent number of water molecules were deleted from the system (Fig. 2.5). The reactive cut-off distance was increased during the networking formation from 3 to 6 Å.

Finally, steps 3 and 4 were repeated until no more pairs of reactive atoms satisfying all criteria were detected in the system.

According to the procedure outline above, a hybrid O/I 3D system based on GPTMS was successfully generated with high conversion. It is well known that a 100 % conversion is rarely achieved experimentally because of gel transition at later stage. Although other systems with a different (lower) conversion degree 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 $\alpha = 0.9$. 

Fig. 2.4 Geometry-optimized molecular model of the GPTMS molecule, along with the atom labelling used in this work. All atoms are in stick-and-ball representation. *Colour code: Si light grey; O black; C dark grey, H white*
The central unit cells of the initial GPTMS monomers, and the final network systems are shown in Fig. 2.6. As can be seen, the 3D network structures are characterized by the presence of both chemical and physical crosslinks. Some bonds clearly connect to image cells across the boundary and thus extend throughout the periodic system.

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. Accordingly, a high molecular weight branched polysilsesquioxanes (PSSQOs)—

<table>
<thead>
<tr>
<th>Table 2.1 Geometrical parameters of the GPTMS molecular model after geometry optimization with COMPASS FF</th>
</tr>
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<tbody>
<tr>
<td>Si–O1(O2,O3)/Å</td>
</tr>
<tr>
<td>Si–C1/Å</td>
</tr>
<tr>
<td>H1–O1/Å</td>
</tr>
<tr>
<td>C1–C2/Å</td>
</tr>
<tr>
<td>C2–C3/Å</td>
</tr>
<tr>
<td>C3–O4/Å</td>
</tr>
<tr>
<td>O4–C4/Å</td>
</tr>
<tr>
<td>C4–C5/Å</td>
</tr>
<tr>
<td>C5(C6)–O5/Å</td>
</tr>
<tr>
<td>C5–C6/Å</td>
</tr>
<tr>
<td>H4–C1/Å</td>
</tr>
<tr>
<td>H12–C5/Å</td>
</tr>
</tbody>
</table>

Atom numbering as in Fig. 2.4

Fig. 2.5 Details of the GPTMS molecular modelling showing, in stick-and-ball representation, the reactive atom pairs (a), and the newly formed Si–O–Si bond and the corresponding deleted water molecule (b). All other atoms are in line rendering. Colour code: Si light grey; O black; C dark grey, H white
generic products obtained by the hydrolytic condensation of monomers such as GPTMs—structure grows, until a gel system is formed at a conversion degree approximately equal to 0.7. The corresponding composition of the gel state exhibits a considerable amount of silicon atoms involved in triple intermolecularly branched units representing the crosslinks in the network. Further SAXS experiments revealed also that, under acid catalysis, no microphase separation resulting in self-assembly of regularly arranged domains is present [44]. Contrarily, a broad distribution of high molecular weight structure with dangling organic substituents is formed, the structure not promoting any ordering. The inspection of the 3D structures obtained from the simulation procedure compares well with the network picture described above. Indeed, the overall network structure is linear and extends in all three directions, with presence of unstrained rings with a number of Si atoms greater than 4. To further confirm the quality of the network structures, Table 2.2 lists the mean values of some geometrical parameters, as obtained by averaging over 10 MD frames. By comparing these data with the corresponding geometrical features of the GPTMS monomer model reported in Table 2.1, we can see that the differences are rather small, indeed confirming that crosslinking does not result in considerable geometrical modifications, and no substantial strain is induced in the final network.

2.3.2 3D Network Relaxation for Thermophysical Properties Determination

After the GPTMS 3D network structures were built starting from the two partial charge scheme and applying the procedure detailed above, each system was subjected to further annealing cycles up to 600 K. The minimum energy structure for each system was selected for further NVT and NPT molecular dynamics simulation at 300 K for data collection. The final density of the MD-equilibrated systems corresponding to the two different atomic partial charge schemes, AM1-ESP and COMPASS, respectively, is reported in Table 2.3 where it can be seen that the equilibrated network densities obtained from initial structure modelled with both partial charge schemes are utterly similar. Further, starting from two different annealed initial GTPMS 3D boxes (i.e. structure I and structure II) leads to the same network final density values, thus validating the initial structure selection protocol.

2.3.3 Mechanical Properties (Elastic Constants) Determination

The mechanical behaviour of a given molecular system can be described by using continuum mechanics. Since, however, any molecular system has a discrete
structure, the model to be employed for the estimation of the elastic constants is an equivalent-continuum model, in which the overall mechanical response of representative volume elements to an applied set of boundary conditions is equivalent to the response of the molecular representative volume system subjected to the same set of boundary conditions. The equivalent-continuum is assumed to have a linear–elastic constitutive behaviour. The generalized constitutive equation of the equivalent continuum hence is given by

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$$

(2.1)

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Table 2.2 Mean geometrical parameters of the GPTMS 3D network obtained from structure optimized with the COMPASS atomic partial charges scheme by averaging over 10 MD frames

<table>
<thead>
<tr>
<th></th>
<th>Si–O/Å</th>
<th>Si–C1/Å</th>
<th>O–Si–O</th>
<th>O–Si–C</th>
<th>Si–C–C</th>
<th>Si–O–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.660</td>
<td>1.928</td>
<td>124.1°</td>
<td>104.3°</td>
<td>123.5°</td>
<td>142.8°</td>
</tr>
</tbody>
</table>

Table 2.3 MD-equilibrated density values $\rho$ for the 3D GPTMS-based O/I network structures obtained from the simulations

<table>
<thead>
<tr>
<th>Atomic partial charge scheme</th>
<th>Initial structure I $\rho$ (g/cm$^3$)</th>
<th>Initial structure II $\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AM1-ESP$</td>
<td>1.368</td>
<td>1.369</td>
</tr>
<tr>
<td>$COMPASS$</td>
<td>1.371</td>
<td>1.368</td>
</tr>
</tbody>
</table>

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Fig. 2.6 (a) Central unit cell of the initial GPTMS monomers. (b) Hybrid I/O 3D network structure obtained starting from the GPTMS simulation cell (a) and applying the procedure described in the text [45]
where $\sigma_{ij}$ are the components of the stress tensor ($i, j = 1, 2, 3$), $C_{ijkl}$ are the components of the linear–elastic stiffness tensor, and $\varepsilon_{kl}$ are the components of the strain tensor. It is further assumed that the system has isotropic material symmetry. In atomistic calculation, the internal stress tensor in a system can be obtained using the virial expression:

$$\sigma = -\frac{1}{V_0} \left[ \left( \sum_{i=1}^{N} m_i (v_i v_i^T) \right) + \left( \sum_{i<j} r_{ij} f_{ij}^T \right) \right]$$

(2.2)

where index $i$ runs over all particles through $N$, $m_i$ and $v_i$ are the mass and the velocity of the particle, respectively, $f_i$ is the force acting on the particle, and $V_0$ is the undeformed system volume.

Two classes of methods for calculating material elastic constants using molecular simulations are available in the literature at present. Consistently, the static method (i.e. based on molecular mechanics) was found to be more practical and reliable than the one based on molecular dynamics. Thus, a constant strain minimization method, belonging to the class of static methods, was applied to the equilibrated 3D O/I network system. Accordingly, after an initial system energy minimization, three tensile and three pure shear small deformations (to remain within elastic limits) are applied. The system is then again energy minimized following each deformation. The stiffness matrix is calculated from the second derivative of the potential energy $U$ with respect to strain $\varepsilon$ as follows:

$$C_{ij} = \frac{1}{V} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} = \frac{\partial \sigma_i}{\partial \varepsilon_j} = \frac{\sigma_{i+} - \sigma_{i-}}{2 \varepsilon_j}$$

(2.3)

where $\sigma_i$ is the $i$th component of the internal stress tensor and $\sigma_{i+}$ and $\sigma_{i-}$ are the components associated with the stress tensor under tension and compression, respectively. The Lamé constants for the structure—$\lambda$ and $\mu$—can in turn be calculated from the related stiffness matrix:

$$\lambda = \frac{1}{3} (C_{11} + C_{22} + C_{33}) - \frac{2}{3} (C_{44} + C_{55} + C_{66})$$

(2.4)

$$\mu = \frac{1}{3} (C_{44} + C_{55} + C_{66})$$

(2.5)

For isotropic materials, the stress–strain behaviour can finally be described in terms of the Lamé constants according to the equations:

$$E = \mu \frac{3\lambda + 2\mu}{\lambda + \mu}$$

(2.6)

$$G = \mu$$

(2.7)
\[ B = \lambda + \frac{2}{3} \mu \] 
\[ v = \frac{\lambda}{2(\lambda + \mu)} \]

where \( E, G, B, \) and \( v \) represent Young’s modulus, shear modulus, bulk modulus, and Poisson’s ratio, respectively.

The mechanical properties calculated using the 3D network structures obtained from the MD simulations are reported in Table 2.4. The second column refers to the properties of the network structures simulated with the partial charge scheme obtained using the AM1-ESP approach, while the third column lists the same quantities resulting from the 3D structures bearing the partial charges as assigned by the COMPASS force field. In the last column of this Table, the range of experimental values of the corresponding mechanical properties \([47, 48]\) is also reported for comparison.

The data in Table 2.4 indicate that the charging method has a certain impact on the mechanical properties of the final material. Indeed, in the case of the AM1-ESP partial charging scheme, the values obtained from the simulation are located close to the lower limit of the expected range, if not below. With the COMPASS force field \([46]\) charge scheme, the mechanical characteristic of the GPTMS network lays in the expected range. Although no experimental measures are available for our systems, as a conclusion, we could say that the predictions obtained by using a standard force field satisfactorily reproduce the available mechanical experimental data.

### 2.3.4 Constant-Pressure and Constant-Volume Heat Capacity Determination

Statistical fluctuations about the mean values of quantities measured during the course of an MD simulation can be directly related to thermodynamic properties. Besides common average quantities like density, pressure, or energy, the analysis of fluctuations allows to determine properties like heat capacities, compressibility, thermal expansion coefficient, or the Joule–Thomson coefficient. Specific heat capacity at constant pressure \( C_P \), for instance, is obtained from the fluctuations of energy in the isothermal–isobaric ensemble (NPT) according to

\[ C_P = \frac{1}{k T^2} \left\langle \delta(K + U + pV)^2 \right\rangle \] 

where \( k \) is the Boltzmann constant, \( K \) and \( U \) denote the instantaneous values of the kinetic and potential energy, respectively, and \( T, P, \) and \( V \) are the familiar
thermodynamic state variables. In addition, the notation $\delta X$ stands for $X - \langle X \rangle$, where $\langle X \rangle$ denotes the ensemble average value of a given quantity $X$.

The specific heat capacities at constant volume and constant pressure, $c_v$ and $c_P$, calculated for the GPTMS-based O/I network are reported in Table 2.5. Again, these properties were obtained for structure bearing the two different partial charge schemes. In the last column, the experimental data range available in the literature for similar systems is also shown for comparison [47, 48]. As seen for the mechanical properties, all data calculated starting from structures bearing atomic partial charges derived from the AM1-ESP approach lay in the lower limit of the experimental data range, while those obtained from the COMPASS partial charge set fall better within the interval of observed values.

### Table 2.4

<table>
<thead>
<tr>
<th></th>
<th>Structure I</th>
<th>Structure II</th>
<th>Structure I</th>
<th>Structure II</th>
<th>Experimental data$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AM1-ESP</td>
<td>AM1-ESP</td>
<td>COMPASS</td>
<td>COMPASS</td>
<td></td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>2.85</td>
<td>3.00</td>
<td>3.52</td>
<td>3.96</td>
<td>1.9–4.5</td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>1.89</td>
<td>2.00</td>
<td>2.58</td>
<td>2.66</td>
<td>2.5–7.0</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>1.14</td>
<td>1.20</td>
<td>1.38</td>
<td>1.58</td>
<td>0.9–1.5</td>
</tr>
<tr>
<td>$\nu$ (−)</td>
<td>0.25</td>
<td>0.27</td>
<td>0.27</td>
<td>0.25</td>
<td>0.3–0.4</td>
</tr>
<tr>
<td>$\lambda$ (GPa)</td>
<td>1.13</td>
<td>1.20</td>
<td>1.66</td>
<td>1.61</td>
<td>–</td>
</tr>
<tr>
<td>$\mu$ (GPa)</td>
<td>1.14</td>
<td>1.20</td>
<td>1.38</td>
<td>1.58</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Average values for crosslinked networks

2.3.5 Properties Estimated at Atomistic Level as a Function of the Degree of Reticulation $\alpha$

It is also interesting to investigate thermomechanical properties as a function of the degree of reticulation $\alpha$ (Fig. 2.7). The morphologies obtained from the simulations are reported in Fig. 2.8 as a function of the degree of reticulation $\alpha$.

2.4 Mesoscale Simulation for the Determination of the Nanostructures

Mesoscale simulation aims at predicting the morphology of the systems at a much larger scale than the atomistic one. This is accomplished by grouping atoms or molecules in beads, assigning an interbead potential to each bead, and looking at the time evolution of the system until equilibrium is reached. The nanostructure
Table 2.5 Specific constant-pressure ($c_p$) heat capacity for the 3D GPTMS-based O/I network structures obtained from the MD simulations

<table>
<thead>
<tr>
<th>Specific heat capacity</th>
<th>Structure I</th>
<th>Structure II</th>
<th>Structure I</th>
<th>Structure II</th>
<th>Experimental data$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$ (kJ/kgK)</td>
<td>AM1-ESP</td>
<td>AM1-ESP</td>
<td>COMPASS</td>
<td>COMPASS</td>
<td>1.1–2.2</td>
</tr>
<tr>
<td>1.16</td>
<td>1.23</td>
<td>1.64</td>
<td>1.49</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Average values for crosslinked networks

Fig. 2.7 Young’s modulus ($E$) (a), heat capacity ($C_p$) (b), and linear expansion coefficient ($\beta$) (c) calculated from atomistic simulations as a function of the degree of reticulation $\alpha$

Fig. 2.8 Morphologies at different degree of reticulation. a $\alpha = 0.3$; b $\alpha = 0.5$; c $\alpha = 0.7$; d $\alpha = 0.9$
obtained at equilibrium will be the basis of finite-element calculations for the estimation of the final macroscopic properties. As mentioned above, several simulation methods are available at mesoscale: among other, dissipative particle dynamics (DPD) is the most suitable for describing sol–gel nanocomposites.

### 2.4.1 DPD Theory

In the DPD simulation method [24–26], a set of particles moves according to Newton’s equation of motion and interacts dissipatively through simplified force laws. If the mass of all particles is set equal to unity, the time evolution of the positions \( \mathbf{r}_i(t) \) and momenta \( \mathbf{p}_i(t) \) is given by the well-known relationships:

\[
\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i(t) \quad \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i(t)
\]  

(2.11)

where \( \mathbf{r}_i, \mathbf{v}_i, \) and \( \mathbf{f}_i \) are the position vector, velocity, and total force, respectively, acting on particle \( i \).

The force acting on the particles, which is pairwise additive, can be decomposed into three elements: a conservative \( \mathbf{F}_{ij}^C \), a dissipative \( \mathbf{F}_{ij}^D \), and a random \( \mathbf{F}_{ij}^R \) force. Accordingly, the effective force \( \mathbf{f}_i \) acting on a particle \( i \) is given by

\[
\mathbf{f}_i = \sum_{i \neq j} \left( \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right)
\]  

(2.12)

where the sum extends over all particles within a given distance \( r_c \) from the \( i \)th particle. This distance practically constitutes the only length scale in the entire system. Therefore, it is convenient to set the cut-off radius \( r_c \) as a unit of length (i.e. \( r_c = 1 \)), so that all lengths are measured relative to the particle’s radius.

The conservative force is a soft repulsion, given by

\[
\mathbf{F}_{ij}^C = \begin{cases} 
  a_{ij} (1 - r_{ij}) \hat{\mathbf{r}}_{ij} & (r_{ij} < 1) \\
  0 & (r_{ij} \geq 1)
\end{cases}
\]  

(2.13)

where \( a_{ij} \) is the maximum repulsion between particles \( i \) and \( j \), \( r_{ij} \) is the magnitude of the particle–particle vector \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) (i.e. \( r_{ij} = |\mathbf{r}_{ij}| \)), and \( \hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij} / r_{ij} \) is the unit vector joining particles \( i \) and \( j \). The other two forces, \( \mathbf{F}_{ij}^D \) and \( \mathbf{F}_{ij}^R \), are both responsible for the conservation of the total momentum in the system and incorporate the Brownian motion into the larger length scale. They are given by the following expressions:
\[ F_{ij}^D = -\gamma \omega^D r_{ij}(\hat{r}_{ij} \cdot \mathbf{v}_{ij}) \hat{r}_{ij} \]
\[ F_{ij}^R = \sigma \omega^R r_{ij} \theta_{ij} \hat{r}_{ij} \]

(2.14)

where \( \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \), \( \omega^D \) and \( \omega^R \) are \( r \)-dependent weight functions tending to zero for \( r = r_c \), and \( \theta_{ij} \) is a randomly fluctuating variable with zero mean and unit variance. Español and Warren [49] have shown that one of the two weight functions in Eq. (2.4) can be chosen arbitrarily, thereby fixing the other weight function. However, the weight function and constants should obey

\[ [\omega^R(r)]^2 = \omega^D(r) \quad \sigma^2 = 2\gamma k_B T \]

(2.15)

where \( k_B \) is the Boltzmann constant.

In the DPD model, individual atoms or molecules are not represented directly by the particle, but they are coarse-grained into beads. These beads represent local “fluid packages” able to move independently. Incorporation of chain molecules simply requires the addition of a harmonic spring force between the beads:

\[ F_{ij}^{\text{spring}} = K r_{ij} \]

(2.16)

By means of this spring, the beads can interconnect to highly complex topologies. In this work, however, the calculations are performed with linear chains only.

### 2.4.2 Reactive Dissipative Particle Dynamics

At the mesoscale level, we employed the so-called reactive dissipative particle dynamics (RxDPD) simulation technique. The RxDPD method is primarily intended for the prediction of the system composition and the thermodynamic properties of reaction equilibrium polymer systems. The RxDPD formulation has been developed and validated by Lisal and co-workers [50, 51].

This approach combines elements of dissipative particle dynamics (DPD) and reaction ensemble Monte Carlo (RxMC) [52, 53] for the mesoscale simulation of reaction equilibrium polymer systems and utilizes the concept of a fractional particle [54]. The fractional particle is coupled to the system via a coupling parameter that varies between zero (no interaction between the fractional particle and the other particles in the system) and one (full interaction between the fractional particle and the other particles in the system). The time evolution of the system is governed by the DPD equations of motion, accompanied by changes in the coupling parameter. The coupling-parameter changes are either accepted with a probability derived from the grand canonical partition function or governed by an equation of motion derived from the extended Lagrangian. The coupling-parameter changes mimic
forward and reverse reaction steps, as in RxMC simulations. The RxMC method is a powerful molecular-level simulation tool for studying reaction equilibrium mixtures. The method only requires inputting the interaction potentials and the ideal-gas properties of the reaction species that are present. Most notably, the method does not require a reactive-type potential that mimics bond breakage and formation. Reactions are simulated by performing forward and reverse reaction steps according to the RxMC algorithm which guarantees that the reaction equilibrium conditions are satisfied.

The DPD simulation of crosslinked polymeric matrices and nanoparticles requires incorporating a non-crossing condition by adding bond–bond repulsion to the model [55]. The distance of closest approach between two bonds, \( D \), is computed, and a repulsive interaction is then applied based on \( D \). The form of the bond–bond repulsion potential, \( u_{\text{rep}}(D) \), avoiding artificial bond crossing in DPD simulation was given by Pan and Manke [56].

\[
  u_{\text{rep}}(D) = \frac{K_{\text{rep}}}{2} D_c \left( 1 - \frac{D}{D_c} \right)^2 (D < D_c)
\]  

(2.17)

where \( K_{\text{rep}} \) is the bond–bond repulsion constant, \( D_c \) is the bond–bond cut-off distance and \( D = P_i + t_iR_i - (P_j + t_jR_j); P_i \) and \( P_j \) are midpoints of bonds \( i \) and \( j \), respectively, \( R_i \) and \( R_j \) are the vectors characterizing the direction and length of each bond, and \( t_i \) and \( t_j \) are parameters which indicate where we are along each bond. The bond–bond cut-off distance was set approximately equal to \( 0.15r_c \) and the bond–bond repulsion constant to \( \approx a_{ij} \) of the specie involved in the bonds.

Crosslinking of polymeric matrix is mimicked by a reactive potential

\[
  u_{\text{reac}} = \varepsilon \exp \left[ -\frac{(r_{ij} - r_w)^2}{\lambda^2} \right]
\]  

(2.18)

where \( \varepsilon \) is the Gaussian well \( (\varepsilon = 2) \) and \( r_w \) and \( \lambda \) are its position and width, respectively. The polymer Gaussian well position corresponds to \( r_w = 0.6 \) and the polymer Gaussian well width \( \lambda \) to \( (\lambda/r_c)^2 = 0.003 \).

The mass of DPD beads \( m_i \), \( r_c \), and \( kT \) are used as the unit of the mass, length, and energy, respectively; \( k \) is the Boltzmann constant, and \( T \) is the temperature.

### 2.4.3 Dissipative Particle Dynamics: Simulation Details and Results

In order to calculate mesoscale interaction parameters, MD simulations were used to predict the equilibrium conformation and the interaction energy values for the ternary GPTMS-MPTMS/ZnS nanocomposite. All atomistic simulations were performed using Materials Studio (v 5.5 Accelrys, San Diego, CA). As far as the
ZnS (sphalerite) model is concerned, starting from relevant crystallographic coordinates [57], we built the unit cell using the Crystal Builder module of Materials Studio. We chose sphalerite as it is recognized as the most stable phase of zinc sulphide polymorphs, and for the same reason, we selected the (110) surface. We replicated the basic cell in order to obtain a super cell of approximately $3.2 \times 3.2 \times 1.1$ nm$^3$ size ($6 \times 6 \times 2$).

Then, we modelled the surface modifier, chosen to be a (3-mercaptopropyl) trimethoxysilane (MPTMS) molecule. The modifier conformational search was carried out using COMPASS FF, and applying our validated combined molecular mechanics/molecular dynamics simulated annealing (MDSA) protocol [58–67]. More details on the atomistic simulation for the determination of the interaction energies are reported in [68]. By definition, the binding energy $E_{\text{bind}}$ is the negative of the interaction energy. As an example, to calculate the binary binding energy term $E_{\text{bind}}(\text{GPTMS/MPTMS})$, we first created a GPTMS–MPTMS system, deleting the ZnS surface from the equilibrated MD trajectory frames, and then calculated the potential energy of the system $E_{\text{GPTMS/MPTMS}}$. Next, we deleted the MPTMS molecules, leaving the GPTMS network alone, and thus calculated the energy of the GPTMS matrix, $E_{\text{GPTMS}}$. Similarly, we deleted GPTMS from the GPTMS–MPTS system and calculated $E_{\text{MPTMS}}$. Then, the binding energy $E_{\text{bind}}(\text{GPTMS/MPTMS})$ is simply obtained from the following equation:

$$E_{\text{bind}}(\text{GPTMS/MPTMS}) = E_{\text{GPTMS}} + E_{\text{MPTMS}} - E_{\text{GPTMS/MPTMS}}$$

The remaining binding energy terms $E_{\text{bind}}(\text{GPTMS/ZnS})$ and $E_{\text{bind}}(\text{MPTMS/ZnS})$ can be calculated in an utterly analogous fashion from the corresponding energy components. Figure 2.9 shows one snapshot taken along the equilibrated MD trajectory as an example.

As the simulation proceeds in time, the modifier molecules partially shield the surface from the interaction with the matrix and at the same time interpenetrate the polymeric network by virtue of favourable interaction energies. Following our previous work originally based on Tanaka’s approach [58–67], we derived interaction energies as well as the binding energies from the equilibrium conformation of the corresponding MD simulations. The values obtained are reported in Table 2.6.

The binding energies between the individual components constitute the input parameters for the calculation of the mesoscopic corresponding interaction parameters. We then used RxDPD to model crosslinked polymeric matrices and nanoparticles at mesoscale level.

Our mesoscopic system consists of coarse-grained polymers and coarse-grained nanoparticles. Nanoparticles are modelled by icosahedrons, i.e. an assembly of 13 mesoscopic beads connected by harmonic spring potentials. Figure 2.10 shows schematically mesoscopic model for the nanoparticles. This effectively represents a uniformly dispersed set of nanoparticles of approximately 5–6 nm in diameter. Ideally, inorganic particles for optical applications should have a diameter below 10 nm; this is because the presence of even a small percentage of particles or
aggregates larger than 100 nm results in strong light scattering in the visible region, causing haze or even turbidity [69, 70]. Consequently, the size of inorganic nanoparticles employed for fabricating high-RI nanocomposites is frequently below 10 nm.

Table 2.6  Equilibrium binary binding energies

<table>
<thead>
<tr>
<th></th>
<th>E_{bind}</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GPTMS-ZnS</td>
<td>$-80.14 \pm 3.57$</td>
<td>GPTMS-MPTMS</td>
<td>$-158.25 \pm 8.19$</td>
</tr>
<tr>
<td>MPTMS-ZnS</td>
<td>$-60.24 \pm 4.56$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All energies are expressed in kcal/mol, and standard deviations are reported in parenthesis.

Fig. 2.9  Frame extracted from the equilibrated MD trajectory of a system made up of a ZnS surface chemically modified with MPTMS molecules and a crosslinked GPTMS matrix

Fig. 2.10  Mesoscopic model for the nanoparticle used in this work
The polymer is represented by a chain of mesoscopic connected beads; the polymer chains can crosslink via a reactive potential and originate a 3D amorphous network. A ring of four GPTMS monomers constitutes the basic unit, i.e. single DPD bead, for the GPTMS network model at mesoscale. Figure 2.11 shows the mesoscopic model for the GPTMS matrix used in this work.

Assuming this as the basic mesoscale unit for the polymer, we simulated the pure network using the RxDPD technique and we compared the final structure of the network reached after mesoscale and atomistic simulation. As shown in Fig. 2.12, predicted structures resulting from mesoscale crosslinking agree quite well with those obtained by atomistic simulations. In light grey is the probability to find cyclic structures of 4, 8, and 12 units in the atomistic network and in dark grey in the mesoscale network. The agreement between the two distributions means that the mesoscale model chosen for representing the network fits well the atomistic one, thus validating the choice for the mesoscale unit of the matrix.

![Mesoscopic model for the GPTMS matrix used in this work](image1)

![Atomistic/mesoscale comparison of crosslinking resulting structures in GPTMS systems](image2)
As it is easy to understand from the probability distribution, our mesoscale network was essentially constituted by 79 mol% of 4 rings, 10 mol% of 8 rings, and 11 mol% of 12 rings.

Once defined and optimized the mesoscale models and mesoscale species for the constituents, the next important issue is the determination of the bead interaction parameters. The detailed procedure for obtaining the mesoscale interaction parameters from atomistic molecular dynamics binding energies is explained above. We set the bead–bead interaction parameter for the polymer matrix equal to $a_{\text{GPTMS}} = 25.00$ according to an appropriate value for a density value of $\rho = 3$ [58–67]. As we need one more point as reference following our procedure, we calculated the Flory–Huggins interaction parameter for GPTMS and MPTS $Z_{\text{GPTMS-MPTMS}}$ according to a validated procedure of our group [71], and then, we derived the $a_{\text{GPTMS-MPTMS}}$ interaction parameter using the relation proposed by Groot and Warren [25] linking the Flory–Huggins interaction parameter $Z_{ij}$ to the mesoscopic interaction $a_{ij}$. From our calculations, the Flory–Huggins interaction parameter results to be $Z_{\text{GPTMS-MPTMS}} = 0.11$ and the corresponding DPD interaction parameter $a_{\text{GPTMS-MPTMS}} = 25.34$.

Once these two parameters were set, and their values associate with the corresponding values of the self- and mixed rescaled DPD energies, all the remaining bead–bead interaction parameter for the RxDPD simulation could be easily obtained, starting from the atomistic binding energies. According to this procedure, the interaction parameters were set to $a_{\text{ZnS-GPTMS}} = 26.04$ and $a_{\text{ZnS-ZnS}} = 27.01$, incorporating the effect of MPTMS covering into the ZnS contribution.

The macroscopic properties of a composite material intrinsically depend not only on the properties of each constituent, but also on the characteristics of the composite morphology, interfacial interactions, and nanoparticle loading. To elucidate these critical issues, we varied the nanoparticle loading from 2 to 15 % in volume and we analysed the morphology of the resulting composites and the dispersion of the semiconductor in the matrix after crosslinking reaction occurred.

Figure 2.13 shows clustering analysis of ZnS nanoparticles as a function of nanoparticle loading. We found that up to 5 % volume, the nanoparticles are quite well distributed in polymeric matrix, and then, they start clustering. Most likely, the modifier attached on the metal surface is not sufficient to completely shield the ZnS nanoparticles to favourably interact, and consequently, they tend to aggregate when the concentration is increasing.

In order to avoid nanoparticle aggregation and favour dispersion of the nanoparticles in the polymeric matrix, an accurate control and the increase of MPTMS modifier content in the system could improve the dispersion of the metal. Figure 2.14 shows the dispersion of the nanoparticles at 2 % in concentration as obtained from RxDPD simulations as an example of the mesoscale prevision.
2.5 Macroscale Simulation and Thermophysical Properties Calculation

The mesoscale simulation provides a detailed description of the nanostructure. Since in nanotechnology the nanostructure is responsible for the macroscopic properties, it should be used for their estimation. This is accomplished by mapping the results of the mesoscale simulation onto a finite-element method and then solving the Laplace equation taking into account the density distribution of the components.
2.5.1 Finite-Element Models for the Calculation of PCN Effective Properties

The prediction of effective properties for materials characterized by complex microstructural features at the nanoscale such as sol–gel nanocomposites should ideally include information deriving from models developed at the molecular level. The results of a mesoscale simulation under the form of three-dimensional density maps are used as starting point and transformed into a fixed grid for the integration of the equations to determine macroscopical properties. In other words, the method uses a numerical procedure to determine the overall properties of composites with arbitrary morphologies from the properties of the components based on small homogeneous grid elements. The morphology is defined by a number of phases in a periodically continued base cell of cubic or orthorhombic shape where the phases may consist of any material. The resolution depends solely on the number of grid elements used. For each of the grid elements, it is possible to specify the fraction of each phase contained in that particular position. By applying a displacement-based finite-element method to the volume mesh, the responses to external deformations are calculated. In order to calculate mechanical properties, an elastic solver is used. It applies six different infinitesimally small deformations to the composite and minimizes the total strain energy for each of these deformations in order to calculate the elastic composite properties.

The properties of the nanoparticles were taken from the available literature referring to typical characteristics [72, 73] and those of the matrix from our atomistic calculation. Density fields are mapped onto a fixed grid FE model, and properties are assigned to each mesh element accordingly. This method has been implemented in the commercial software MesoProp, which allows the morphology of each phase present in a mesoscale model to be exported, via density field mapping, to a cubic or orthorhombic cell featuring periodic boundary conditions and a fixed tetrahedral mesh. For each mesh element, pure component properties are averaged according to the imported density map (Fig. 2.15), and the effective properties of the entire macrostructure can thus be calculated based on the morphological details of the mesoscale simulation obtained using DPD. The effective properties of the composites could be finally estimated as schematically illustrated in Fig. 2.16.

The pure component input data for the microFEM simulation used in the simulation are reported in Table 2.7. They are estimated according to the following assumptions: (i) GPTMS properties from atomistic simulation, (ii) GPTMS maximum grade of reticulation ($\alpha = 0.93$), (iii) MPTMS same properties of GPTMS, and (iv) 25% MPTMS coverage over the ZnS surface.

Examples of a 3D density distribution are reported in Fig. 2.17 for lower (2 % vol) (a and b) and upper (5 % vol) (c and d) content of nanoparticles.

Accordingly, the macroscopic mechanical properties of the GPTMS–MPTMS/ZnS nanocomposite as calculated from FE analysis are reported in Table 2.8 as function of nanoparticle loading.
Predicted values of mechanical characteristics are in good agreement with those expected for similar or comparable systems [74–76]. The results shown here demonstrate that only 2–5% volume ZnS incorporation into the GPTMS matrix was effective in enhancing the mechanical strength of the material. The reason for that is the high mechanical strength of ZnS ($E = 70$ GPa) and its smaller size allow a greater surface area to be available for the polymer/filler interaction and adhesion.

When the loading is low, due an attractive interaction between the nanoparticles modified and the surrounding polymer, the interphases region has decreased molecular mobility over that of the bulk polymer, and this consequently results in an increase in modulus. Further, the molecular structure of the shell material (MPTMS) provides the compatibilization of the nanoparticles with the polymer to prevent coagulation.

When the nanoparticle loading is increased, this shielding effect is no longer sufficient to avoid particle interaction and aggregation occurs. The presence of clusters at higher percentage of loading explains why the increasing of the

| Table 2.7 Input data for microFEM simulations in the multiscale framework |
|---------------------------|--------------|----------------|----------------|----------------|
|                           | GPTMS        | ZnS-MPTMS      |                |                |
| Young’s modulus (GPa)     | 2.1          | 56.7           |                |                |
| Poisson ratio (−)         | 0.27         | 0.28           |                |                |
| Density (g/cm$^3$)        | 1.370        | 3.410          |                |                |
mechanical properties with the addition of the semiconductor is much lower than the value expected. The presence of clusters in the matrix reduces the volume-to-surface ratio, and the composite behaves as a traditional microcomposite rather than a nanocomposite.

![Fig. 2.17 3D density distribution of GPTMS-MPTMS/ZnS nanocomposite at 2 %vol, (a) and (b), and 15 %vol, (c) and (d), of metal. Particle density is in grey and matrix density in white. Two different visualizations are reported, full cell view (Fig. a, c), and cut plane (Fig. b, d). In all pictures is visible the grid mesh employed for FEM calculation](image)

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<th>Volume loading (%)</th>
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<th>5</th>
<th>10</th>
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<td>Young’s modulus (GPa)</td>
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<td>2.30</td>
<td>2.36</td>
<td>2.52</td>
</tr>
<tr>
<td>Poisson ratio (−)</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>0.87</td>
<td>0.91</td>
<td>0.93</td>
<td>0.99</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>1.61</td>
<td>1.67</td>
<td>1.71</td>
<td>1.83</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1,412</td>
<td>1,473</td>
<td>1,577</td>
<td>1,680</td>
</tr>
</tbody>
</table>
2.6 Conclusions

Sol–gel nanocomposites have attracted significant attention since their structure and properties can be easily manipulated, even at the molecular level, by the precise design and tailoring of the nanoscale building blocks and organic matrix. Although the promising applications of these nanocomposites have facilitated the rapid development of this area in both fundamental and applied research, there are still lots of questions that need to be addressed. The greatest obstacle to the industrial-scale production and commercialization of these nanocomposites is the dearth of cost-effective strategies for controlling the homogeneous dispersion of the nanoscale building blocks in polymer hosts, especially when high inorganic loading is used. The ex situ method is still considered to be a facile and feasible route for the generation of high-refractive index nanocomposites; nevertheless, the key challenge is to carry out the large-scale preparation of high-refractive index nanoparticles with good compatibility with polymer matrices or monomers. Another hurdle to the broader use of the high-refractive index nanocomposites is the lack of a structure-property relationship because there are limited property databases for these nanocomposites. Thus, greater efforts are needed to correlate the structure of the nanocomposites with their macroscopic performance, including optical properties, thermal and mechanical properties, light stability, and processibility, which is very important for the precise design of nanomaterials with excellent balanced properties.

In this contribution, the power of integrating modelling across different scales and with experimental data has been demonstrated in the area of sol–gel nanocomposites of industrial interest and application. Further, we proposed an alternative and promising route, system independent, linking through the scales. Developing such a multiscale method is very challenging but indeed represents the future of computer simulation and modelling, whatever the target field of application is. New concepts, theories, and computational tools should be developed in the future to make truly seamless multiscale modelling a reality. Such development is crucial in order to achieve the long-standing goal of predicting particle–structure–property relationships in material design and optimization.

References

Sol-Gel Nanocomposites
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