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# Strategies for the assessment of nanocomposite mechanical properties

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ABSTRACT

The assessment of nanocomposite mechanical properties is a challenging task. Due to their hierarchical structure, which spans from nano to macro length-scales, a different way of thinking from traditional approaches is needed to account for the characteristic phenomena of each length-scale and bridge their effects from the smaller scale to the macroscale.

In the present work, some important issues of nanocomposite modelling are discussed. Then, a classification of the available modelling strategies is proposed, according to the scale from which the problem is addressed. This comprehensive analysis is thought as a necessary tool for the development of new effective approaches.

## 1. Introduction

Thanks to their *hierarchical structure* encompassing different time and length scales, nanocomposites are endowed with properties that are not just a synergistic combination of those pertinent to bulk constituents, rather, a set of new ones coming from the exploitation of matter at its molecular state.

Together with their outstanding properties, one of the most interesting features concerned with the addition of nanofillers is that they offer exceptional improvements at much lower concentrations than traditional (micro-sized) fillers assisting in the achievement of high-level performances across various engineering applications. This is a considerable advantage since lower filler contents translate into lighter composites, which is a desirable feature in many applications [1].

The extraordinary physical and chemical properties of nanocomposites can be related to the so called “nano-effect”, a consequence of the hierarchical structure of this kind of materials. As a matter of facts, a uniform dispersion of nanoreinforcements produces an enormous interfacial area per unit volume (*SSA*) no matter the filler geometry [1–4]. Moreover, as the reinforcement dimensions are of the same length scale as the radius of gyration of polymeric chains, molecular interactions with the matrix cause the formation of an interphase “layer”. Its properties can be very different from those of the constituents as reported in Refs. [5–10] among the others. Given the huge amount of interacting surface, the interfacial area is very large [2–5] so that the whole matrix, or a large part of it, may be essentially considered as interphase material displaying peculiar characteristics.

Focusing on the structural properties of nanocomposites, the literature reports a large amount of data on improvements of stiffness, strength and toughness [1–5,11–20]. The improvement of polymer toughness, in particular, not only broadens the polymer field of structural applications but also makes the use of nanocomposite systems as matrices for fibre reinforced composites a smart solution. As a matter of facts, while they already are a class of materials of industrial appeal, nanomodified polymers can be the basis for the development of ternary namomodified laminates (resin + nanofiller + fibres) through which all the benefits tied to the presence of a “many scale” reinforcement can be synergistically exploited [21–27] (Fig. 1).

A successful engineering application of nanocomposites requires models capable of accounting for their inherent *hierarchical structure* which encompasses the nano and the macro length-scales. An effective modelling should take into account the characteristic phenomena of each length-scale and bridge their effects from the smaller scale to the macroscale. Accordingly, a different way of thinking with respect to the traditional approaches is needed. In micromechanics, indeed, one is used to address to problems concerning with two different characteristic lengths at most (microscale and macroscale) both reasonably described by means of continuum mechanics. Regarding nanocomposites, the presence of three main length-scales (nano-, micro- and macroscale) all of which characterized by peculiar mechanisms, urges a more flexible way to address the problem. Indeed, while modelling molecular interactions between the nanofiller and the matrix would require a discrete approach, the introduction of such an atomistic model up to macro length-scales is limited by the impracticability of

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accounting for more than some hundred millions of atoms. To give an idea of the size of the problem, it is useful to remind here that a nanoclay cluster with a diameter of 0.5 μm and 100 layers has about 85 million atoms [28]. This fact gives rise to the need of a multiscale modelling, each dominant mechanism being studied by means of the best suited model with reference to the given length and time scales. The more a model is able to account for these features, the more it moves from a microscale towards a nanoscale perspective.

Most of the several modelling strategies published in the recent literature are focused on the assessment of nanocomposite elastic properties; however, a comprehensive analysis aimed to identify their main features is still missing.

This represents indeed a necessary condition for the development of new effective approaches.

It is in this perspective that this work is intended with a twofold aim:

- introducing and discussing the main issues of nanocomposite modelling.
- proposing a classification of the available modelling strategies as a function of the scale used to address the problem.

To this end, the main features of each approach are briefly analysed and significant examples available in the literature are presented as well.

## 2. Some important issues in nanocomposite modelling

The reduction of the filler size is the key issue of the extraordinary properties of nanocomposites. In this section the most important features related to the enormously increased specific surface area (*SSA*) to be accounted for modelling are briefly discussed.

### 2.1. Agglomeration

Experimental evidence clearly shows that one of the major limits for the full exploitation of nanocomposite performances, either structural or functional, is the nanofiller agglomeration [3,4,21]. A proper distribution and dispersion is essential to get high *SSA*, which would be compromised by the emergence of clusters. A large particle density reduces the load transfer from the matrix to the nanofillers by strain shielding [29] and affects the overall elastic properties as well as the efficacy of some energy absorbing mechanisms. Notwithstanding this, agglomerates can still have a stiffening effect as recently shown by Dorigato et al. [30].

Moreover, in the authors' opinion, agglomeration may promote mechanisms like *crack pinning* and *crack deflection* which would not take place otherwise due to the size of the nanoreinforcement with respect to the size of the crack front [31,32]. This may positively affect the cyclic resistance to crack propagation [15].

### 2.2. Morphology

The properties of polymer nanocomposites are highly related to their overall morphology. Focusing on polymer layered silicate (PLS) nanocomposites, for instance, three different morphologies are thermodynamically achievable [16] depending on the interplay between the polymer matrix and layered silicates (organomodified or not) and also on the volume fraction of the nanofiller and the processing conditions. There are *separated*, *intercalated* and *exfoliated* or *delaminated nanocomposites*.

In the authors' opinion, being macroscopic properties largely influenced by the overall morphology, its modelling is basic and the research scope should be at least twofold. On the one hand, there is an evident need for understanding the effects of various factors such as the size and shape of the nanofiller, its clustering and the polymer architecture (e.g. homopolymer vs. copolymer) on morphology. On the other hand, once morphology is fully determined, capturing its effects on macroscopic properties by means of effective modeling is likewise important. Moreover, it is worth noting that also the nanofiller has its own nanostructure-related morphology. For example single wall carbon nanotubes (SWCNTs) are characterized by different nanotube lengths, diameter and chirality as well as the tube-end configuration (end-caps) and variability is even more pronounced for multiwall carbon nanotubes (MWCNTs) (since they can be considered as a number of nested SWCNTs [2]). The major additional structural parameters include nanotube outer and inner diameter, the number of nested SWCNTs (wall thickness), and the presence of growth-induced configurations, such as bamboo structures [2].

### 2.3. Matrix/nanofiller interface

The interfacial region surrounding the nanofiller is a zone of altered chemistry, chain mobility, degree of cure and cristallinity. Its properties are not just a synergistic combination of whose of each bulk constituent, rather, a set of new ones due to the inherent inter and supra-molecular interactions which can take place at the nano length scale [5–10]. Accordingly, in the authors' opinion, the emergence of large regions of non-bulk polymer, even at low nanofiller volume fractions, could be soundly correlated to the very high performance improvements reported for nanocomposites. For instance, the presence of a zone of chemical alteration can lower the energy barrier for some toughening mechanisms. A reduction of the degree of cross-linking in the interfacial region, indeed, could promote some local ductile behaviour even in a well known brittle material like epoxy, providing an additional energy absorbing mechanism in the form of matrix plastic deformation [33]. In this scenario, the analytical description of the interface and the assessment of the overall properties accounting for the interphase region is of utmost importance.

To capture the influence of the interphase on the overall behaviour of nanocomposites an insightful study at the molecular level must be carried out. However, pursuing this task by means of experimental investigations at the nano-scale is not straightforward, thus urging another way to address the problem. Supported by the acknowledged efficacy in predicting the interfacial characteristics and capturing the effects of intermolecular and supramolecular interactions [8,9,34–42], the authors believe a molecular analysis could be a suitable candidate, on condition that it is supported by an effective scaling up from nano to macro length scales.

## 3. A classification of the different modelling strategies available in the literature

### 3.1. Preliminary remarks

Great efforts have been devoted in the recent literature to develop appropriate models for the assessment of the mechanical properties of nanocomposites, with special focus on elastic properties. The same cannot be said regarding the modelling of toughness and dissipative damage mechanisms, despite of their importance in the view of developing ternary namomodified laminates. A reason is that toughness is inherently more complicated to assess. While for what concerns elastic property prediction, a model can be directly validated by means of macroscopic experimental data, when dealing with toughening mechanisms the processes at the nanoscale not only are difficult to be identified but they also require the observation and the validation at the same length-scale.

Moreover, the dominant mechanisms may change at different nanofiller contents and are influenced by several parameters such as the type of nanoparticle, the dispersion level, the matrix/nanoreinforcement interface, the nanofiller morphology and the loading conditions (quasi-static or cyclic), just to mention a few.

The aim of this section is to carry out a comprehensive analysis of the currently available modelling strategies, which is still missing in the literature. The same basic ideas can then be translated in the assessment of toughness and, consequently, of dissipated energy.

Within this aim, it is first basic to acknowledge that in the most general case three main stages should be addressed in nanocomposite modelling. Each stage might be tackled with the aid of a dedicated model, with the aim to range from the nanoscale to the macroscale:

- *Molecular models.* Starting from the bottom, the chemical–physical interactions arising at the nanoscale can be accounted for by means of discrete methodologies [8,9,43], that allow to predict the time evolution of a system of interacting particles (e.g. atoms, molecules, granules, etc.) and to estimate its physical properties. The most common of these methodologies is Molecular Dynamics (MD) (see, among the others [8,9]).
- *Nanostructural models.* Proceeding from the bottom to the top, there is the need to assess mechanical interactions, which depend on the morphology. This can be achieved by specific nanostructural models for each kind of nanofiller, usually developed within a continuum mechanics-based frame, in order to effectively describe the stress transfer with the matrix.
- *Micromechanical models.* Going further to the top, it is necessary to scale up the nanoscale-related properties to the macroscale or the mesoscale. This can be tackled by means of classical micromechanical relationships, satisfactorily used for conventional composites with micro-sized reinforcements. This last scale-up often needs to exploit the concept of RVE by a finite element model, with the number of DOF much smaller than those required by MD.

Once having identified the main stages and the related models, the large number of published works aimed at assessing nanocomposite properties can be gathered according to how many and which of the mentioned models are used within the strategy. This inherently define the scale from which the problem is addressed (micro, nano and molecular) and, consequently, the effectiveness in the description of the nanoscale.

Then, we propose here a classification of the possible multiscale modelling strategies into three main groups: "*Micromechanical modelling strategies*", "*Nanostructural modelling strategies*" and "*Molecular modelling strategies*". In brief:

- *Micromechanical modelling strategies* represent the simplest way to address the property prediction although often it is not the most effective. They make use of micromechanical models only. Consequently, the matrix and the nanofiller are described by means of Cauchy's continuum mechanics without accounting for interfacial interactions and nanostructure.
- A more insightful investigation is possible through *Nanostructural modelling strategies.* They make use of both micromechanical models and nanostructural models, thus accounting for the effects of the inherent nanostructure on the overall macroscopic properties but not of the chemical–physical interactions.
- Finally, *Molecular modelling strategies*, make a combined use of all the above mentioned models. The scope of the analysis is taken to the actual nanoscale level to account for intermolecular and supramolecular interactions by means of discrete methodologies. Accordingly, the scale-up from nano to macro length scales is not straightforward and requires an effective multiscale approach combining nanostructural and micromechanical models.

The concept of assembling basic models to build a multiscale modelling strategy is defined here as "Three Stage Strategy" (TSS).

A schematic representation of this concept is shown in Fig. 2, while the main characteristics of each strategy are listed in Table 1, together with the relevant advantages and disadvantages. Each strategy is then briefly discussed and representative examples available in the literature are provided as well in next sections. We apologize in advance to all authors who have presented contributions in this field which have not been accounted for in the present paper for reasons of space.

To conclude this section, it is also important to remind that multiscale strategies can be hierarchical or concurrent. In the former case each model is addressed separately, inputs being provided by the solution of the previous model (at the smaller scale). Differently, in the latter case, all the models are solved simultaneously by using inputs from all scales.

However, being easier to be implemented and more efficient from the computational point of view, almost all the available modelling strategies in the literature are hierarchical. For the same reason there are only few examples of concurrent approaches [44,45].

### 3.2. The micromechanical modelling strategy

The micromechanical modelling strategy extends Cauchy's continuum concept to the polymeric chain length-scale. It neglects the nanoscale structure as well as the nanofiller–matrix molecular interactions, and thus fails in capturing the "nano-effect" since it cannot account for the inherent hierarchical structure of the material.

In general, this kind of modelling strategy does not produce reliable predictions of elastic properties, disregarding also the enhanced tendency of the nanofiller to agglomerate [46]. Regarding toughness assessments, micromechanical strategies proved to be incapable of predicting the reported high increments in dissipated energy at low nanofiller volume fractions as documented in [33,47].

In spite of these limitations, micromechanical models, according to the formulation used for conventional composites [48–50], have been applied in the description of some mechanisms like *crack pinning* or *crack deflection* in nanocomposites [33,47].

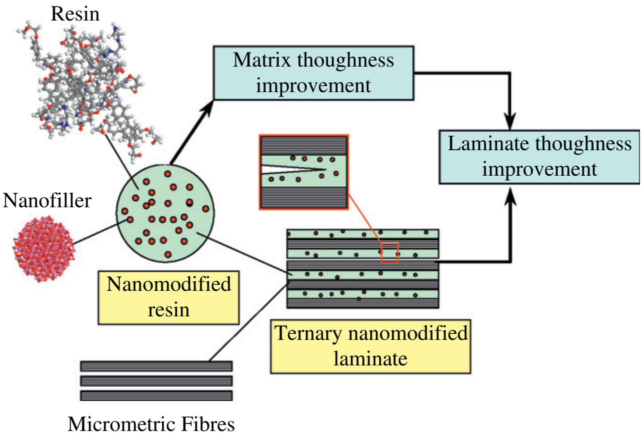

**Fig. 1.** Toughness improvement of ternary laminates through matrix nanomodification.

**Table 1**
Summary of the main advantages and disadvantages related to the different modeling strategies.

| | Micromechanical Strategy | Nanostructural Strategy | Molecular Strategy |
|---|---|---|---|
| **Features** | Nanostructure is neglected | – Continuum nanofiller;<br>– Matrix-nanofiller mechanical interactions are accounted for; | Scaling up from atoms and/or molecules to macro length scale; Physical and chemical interactions are considered; |
| **Advantages** | – Availability of a large bulk of experimental data (at the micrometric level);<br>– Simple analytical expressions;<br>– The overall morphology is accounted for | – Nano scale morphology is accounted for;<br>– Scaling-up from micro to macro with the aid of micromechanical models;<br>– Reasonably reliable predictions; | – The effects of chemical interactions can be fully seized (surfactants etc.);<br>– Mechanical properties of the interphase can be reliably assessed; |
| **Disadvantages** | – The model cannot seize size dependent effects;<br>– Often the predictions are not reliable; | The chemical interactions between filler particles and polymer chains cannot be considered | – Complex molecular models;<br>– High computational power required;<br>– Complex scaling-up; |

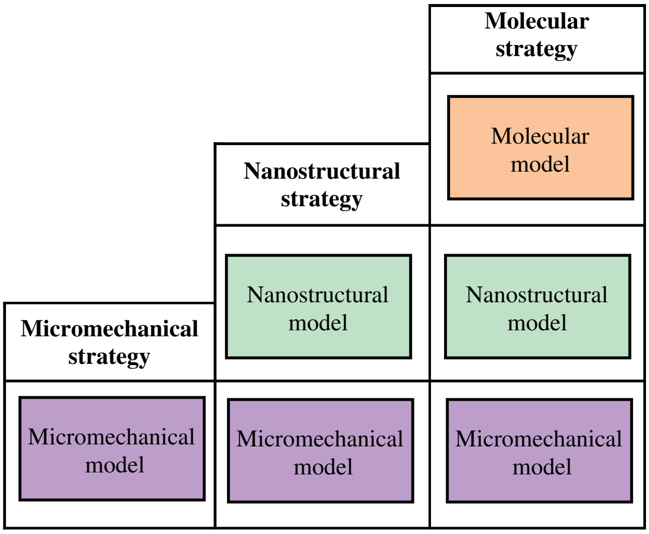

**Fig. 2.** The concept of the “Three Stage Strategy” (TSS): building of modelling strategies from basic models.

For example, while investigating the mechanical properties of alumina nanoparticles reinforced epoxies, Wetzel et al. [33] reported TEM images of the fracture surfaces revealing the emergence of “tail-like” features. Based on this experimental evidence, they suggested to use the micromechanical model formulated for the crack pinning mechanism [48–50] to predict the strain energy release rate of the studied nanomodified system, and compared theoretical predictions with experimental results.

An example of application of this modelling strategy is shown in Fig. 3; data are taken from [33] and refer to $TiO_2$ (diameter: 200–500 nm) and $Al_2O_3$ (primary particles size: 13 nm) nanoparticle reinforced epoxy. Note that in [33] fracture toughness improvements were plotted as a function of nanoparticles diameter to interparticles distance ratio; in Fig. 3, differently, data are plotted as a function of the nanofiller content, as estimated through the following expression:

$$V_f = \frac{\pi}{6} \times \frac{1}{(1 + c/r_0)^3} \tag{1}$$

where $V_f$ is the nanofiller volume content, $r_0$ is the nanoparticle radius and $2c$ is the interparticle distance. Eq. (1) has been obtained assuming a cubic array of nanoparticles.

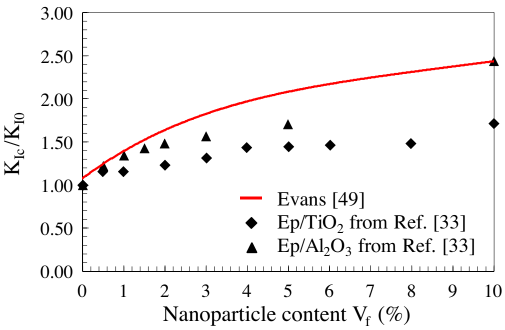

**Fig. 3.** Fracture toughness improvements of $Al_2O_3$ and $TiO_2$ nanoparticles reinforced epoxy. Comparison between experimental results and predictions based on the modelling strategy proposed by Wetzel et al. [33]. Data taken from [33]. $V_f$ according to Eq. (1).

Fig. 3 clearly shows the limits of this strategy, the predicted values exhibiting a far more pronounced energy absorption with respects to those detected experimentally. Indeed, the applied micromechanical model [48–50] does account neither for the size dependency nor for the effects of the region with the altered-chemistry interphase.

### 3.3. *The nanostructural modelling strategy*

The nanostructural modelling strategy represent an attempt of considering the morphology of the nanofiller at the nanoscale while maintaining the hypothesis of continuity.

They start from a specific model of the nanofiller defined “nanostructural”, which allows one to account for its structure at the nanoscale level and the way it mechanically interacts with the matrix. The results of the previous model are implemented in a micromechanical model (e.g. the Mori–Tanaka’s scheme, the Halpin–Tsai equation etc.) often by taking advantage of the concept of an “effective filler” (which allows to account for the actual nanostructure) [51,52]. Alternatively, the scale up can be done by means of full numerical models (e.g. FEA) of a representative volume element (RVE) [53].

An inherent advantage of nanostructural modelling strategies, when compared to micromechanical ones, is that they offer a more insightful analysis of the nanofiller–matrix mechanical interactions without compromising simplicity. As far as elastic properties are concerned, this usually results in more reliable predictions. Of course, since they do not include a molecular model, they cannot account, by nature, for chemical–physical interactions. It is further worth noting that most of the modelling strategies available in the literature can be classified as *Nanostructural*. For the sake of brevity, in the following we will then discuss only two representative examples [51,52] (for further examples see [53–55]).

#### 3.3.1. *Thostenson and Chou’s modelling strategy for the elastic property prediction of MWCNT nanocomposites*

A significant example of a Nanostructural modelling strategy is that due to Thostenson and Chou [51] for epoxy matrix reinforced by aligned MWCNTs.

The main hypotheses of the analysis are a perfect nanotube/matrix adhesion and that only the outer wall of the MWCNT can carry load by neglecting the contribution of the inner layers. In addition, a double Lorentzian distribution of outer diameters is assumed.

The actual filler nanostructure is accounted for by introducing a solid *effective fiber* (see Fig. 4). Through an isostrain condition, the Young modulus of the effective fiber is linked to the outer layer thickness, the outer diameter and the nanotube Young’s modulus.

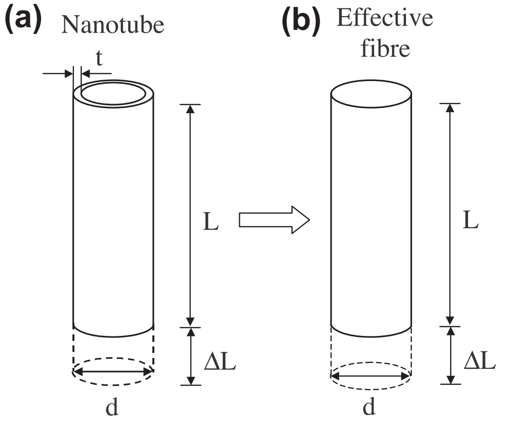

**Fig. 4.** Schematic of (a) nanotube and (b) effective fibre used to model the elastic properties of a nanotube embedded in a composite. (Figure arranged from Thostenson and Chou [51]).

Then, assuming all nanotubes to be perfectly aligned, the Halpin–Tsai micromechanical model is used to determine the longitudinal Young modulus, $E_{11}$ [51].

In this way, $E_{11}$ depends not only on the reinforcement aspect ratio but also on the outer nanotube wall thickness, being then size dependent.

### 3.3.2. Luo and Daniel's modelling strategy for the elastic property prediction of clay nanocomposites

The nanostructural modelling strategy proposed by Luo and Daniel for PLS nanocomposites [52] aims at accounting for the effect of the nanofiller morphology (i.e. its state of intercalation) by means of a three phase Mori–Tanaka model (matrix, exfoliated clays and cluster of intercalated clays).

The properties of intercalated clay clusters are computed by treating them as a system of parallel nanolayers (Fig. 5) assuming an ellipsoidal geometry and the isotropy of each constituent. It is further assumed that the interlayer (intragallery) material has the same Poisson ratio of the bulk matrix, but a Young's modulus $a_m$ times greater, $a_m$ being an intragallery stiffness enhancement factor.

Assuming the in-plane strains (1, 2 directions) and out-of-plane stresses (3 direction) to be the same in both the clay phase and the interlayer matrix, equilibrium and compatibility conditions are used to determine the stiffness tensor of the stack.

The stiffness tensor is found to depend, besides on the clay and the matrix elastic properties, on nanostructural parameters such as the layer thickness to layer spacing ratio and the intragallery stiffness enhancement factor $a_m$ [52].

Finally a three phase Mori–Tanaka's model is used. In more details:

- The exfoliated region is considered as a two-phase system composed of matrix and exfoliated layers, and the stiffener tensor of this simplified system is first determined;
- The exfoliated region is then considered as the effective matrix phase and the intercalated region as the inclusion phase;

In this way, not only the effects of the nanostructure of the clusters but also those of the overall morphology are considered.

An example of application is shown in Fig. 6, where the overall elastic modulus is plotted vs. the nanofiller volume content for different exfoliation ratio, $V_e$. It is evident that the use of $V_e = 10\%$, which is consistent with measured values [52], provides a reasonably good agreement with experimental results for clay epoxy resin.

### 3.4. The molecular modelling strategy

The molecular modelling strategy makes a combined use of the molecular, nanostructural and micromechanical models described in Section 3.1. At the bottom level it abandons the continuity hypothesis in favour of discrete theories; Molecular Dynamics (MD) is an example of these theories.

Molecular modelling strategies are penalized by the elevated computational power required to encompass the different characteristic length-scales, and differ one from the others by the way in which they deal with the property bridging [56–69]. The more elevated computational cost is justified by the need of seizing chemical–physical interactions at the nanoscale, which have a basic influence on functional as well as mechanical properties.

### 3.4.1. Odegard et al. equivalent continuum model for elastic property prediction of MWCNT nanocomposites

An example of Molecular modelling strategy is the *equivalent continuum model* proposed by Odegard et al. [56] for elastic property assessment of MWCNT nanocomposites.

The approach is based on the construction of a unit cell and an equivalent continuum cell, the former one being constituted by a nanotube only and being thought of as a RVE. The initial equilibrium conditions are determined by means of MD analyses.

The continuum cell elastic properties are determined by an Energy Equivalence Rule, which bridges the molecular model to the

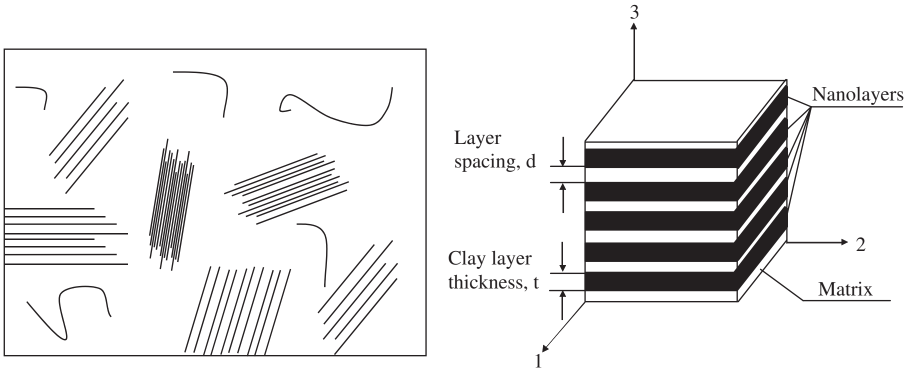

**Fig. 5.** A representative element of an intercalated cluster of clay nanolayers (figure arranged from Luo and Daniel [52]).

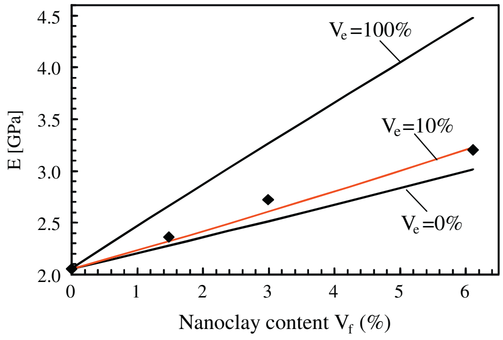

**Fig. 6.** Elastic modulus of nanoclay reinforced epoxy resin. Comparison between experimental results and predictions based on the modelling strategy proposed by Luo and Daniel [52]. Experimentally detected exfoliation ratio $V_e = 10\%$ [52]. (Figure arranged from Luo and Daniel [52]).

equivalent continuum. To do so, an *equivalent truss model* is introduced, in which every intermolecular bond is modelled by a truss pinned in the centres of mass of each particle between the two cells under the same boundary conditions.

Finally, the scale-up to the macroscale is pursued by means of the Mori–Tanaka method, modeling nanotubes as ellipsoidal inhomogeneities with different orientation distributions.

A similar approach has been presented independently by Li and Chou [60] for nanotube elastic property assessment. In this case, each bond is simulated as a beam instead of a truss in order to account also for its flexural rigidity.

### *3.4.2. Scocchi et al. hierarchical modelling for nanocomposites elastic properties*

Other significant examples of Molecular modelling strategy for the prediction of the overall properties of nanocomposites are due to Scocchi et al. [61] and Fermeglia and Pricl [62,63].

The authors propose to bridge the gap between mesoscale and atomistic scale by means of a *Dissipative Particle Dynamics* (DPD) analysis. In the DPD, differently from classical MD, atoms or molecules are not represented directly by a particle but they are coarse-grained into beads (Fig. 7) moving according to Newton's equation of motion and interacting dissipatively through simplified force laws.

The forces acting on each bead are made of three distinct contributions: a conservative, a dissipative and a random force. Each of them is strictly dependent on the interaction energy values to be calculated by means of MD. The required computational power to this end is reduced, as the dimensions of the cell are much lower than those of the mesoscale cell. Accordingly, being the DOF of the system also highly reduced, the simulation can be performed within a mesoscale cell whose dimensions are longer than those commonly set in MD.

The morphology and density fields computed by means of the DPD simulations are then implemented in the FE model of the mesoscale cell. In this way the mechanical properties of mesoscale structures (nanoclay clusters) are determined applying six infinitesimally small deformations and minimizing the resulting total strain energy.

Once the stack properties are calculated, the overall mechanical properties of nanocomposites are calculated by a micro-FE simulation within a RVE. The mechanical properties of the mesostructures of the RVE come from the lower length scale simulations while the overall morphology can be estimated from TEM [61–63].

In this way, the computation of the elastic constants can be performed by the energy minimization described above thus completing the scaling up from the nano to the macroscale.

An example of application of these modelling strategies together with a comparison between experimental and predicted results is shown in Table 2. Data are taken from different references [56,61–63]. It is evident that the adoption of a Molecular Modelling Strategy results in a satisfactory agreement between experimental results and predictions. It is also evident that such strategies are capable to account for the effects of different functionalisation on the overall elastic properties of the nanocomposite.

## 4. Discussion

In this work the main issues concerning the assessment of nanocomposite mechanical properties have been discussed.

One of the reasons of the extraordinary properties of nanocomposites is acknowledged to be the enormous increase in the specific surface area (*SSA*), together with the emergence of molecular interactions at the nanoscale.

However, the resulting multiscale structure makes the problem of predicting nanocomposite properties complicated being it governed by several assorted variables (such as morphology, surface functionalization, nanofiller content, etc.) which do affect different length scales.

The improvement of matrix toughness and all the other weak matrix-controlled properties of composite laminates is the ultimate task of nanomodification. The full exploitation of these benefits requires, however, the development of reliable predictive models. Despite this, while a large bulk of modelling strategies has been proposed in the previous literature to assess elastic properties of nanocomposites, relatively little attention has been paid to strength or toughness assessment.

The analysis carried out in this work highlights the main features of the modelling strategies available up to now as well as

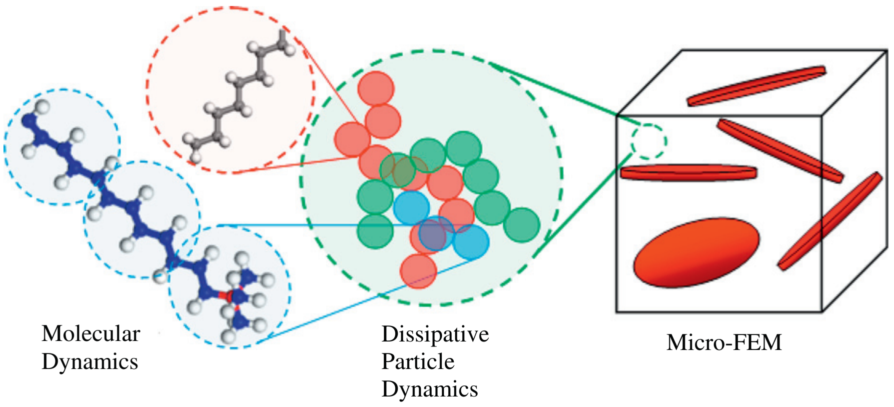

**Fig. 7.** Schematic of the coarse-graining of a surfactant molecules into beads and the following scale up of the density fields computed by means of DPD to the micro-FEM simulation, according to the modelling strategy proposed by Fermeglia and Pricl [63].

**Table 2**
Elastic properties of nanocomposites. Comparison between experimental results and predictions based on different Molecular Strategies.

| System | $V_f$ (%) | Property | Predicted (GPa) | Experimental (GPa) | $\Delta$ (%) | Ref. |
|---|---|---|---|---|---|---|
| Polyimide/SWNT acid treated | 0.2 | E | 1.32 | 1.19 | 11 | [56] |
| Nylon 6/MMT with $M_3C_{18}$ | 1.9 | E | 4.19 | 4.32 | 3 | [61] |
| Nylon 6/MMT with $M_2(C_{18})_2$ | 1.9 | E | 4.41 | 4.60 | 4 | [61] |
| ABS-MMT | 2 | G | 3.15 | 2.75 | 15 | [63] |

their main advantages and disadvantages and can be useful also for the formulation of toughness assessment strategies.

A classification is proposed which gathers the state-of-art strategies into three main groups according to the scale from which the problem is addressed: Micromechanical, Nanostructural and Molecular.

In the authors' opinion the Molecular modelling strategy is the most effective way to tackle the issue of nanocomposite property assessments. Despite of its high computational costs, it represents the only way to account for intermolecular and supramolecular interactions at the nanoscale. By doing so it allows assessing many properties related to chemical–physical interactions, such as the interphase elastic properties, the interfacial energy or the density fields surrounding a nanoparticle, which might have important effects on the overall properties.

The properties coming from the "bottom", which have been computed by a numerical simulation at the nanoscale, can be employed in user-friendly nanostructural and micromechanical models developed within a robust analytical frame.

This is a considerable advantage in the prospect of the engineering of nanostructured materials as relatively simple descriptive models can be obtained.

An example of this concept can be found in Refs. [8,9] where the elastic properties of the interphase surrounding the nanoparticles are first computed by a MD simulation and then employed within a multiphase Mori–Tanaka scheme. A full numerical approach is also possible as well, as documented in [61–63].

In principle, there are substantial differences and difficulties in modelling the elastic constants (small deformations and undamaged material) with respect to the fracture toughness. However a similar strategy can be used to assess toughness improvements and the dissipated energy by dealing with the several parameters affecting the fracture process. In the authors' opinion, this can be achieved by means of a "multi-mechanism" modelling strategy, in which each contribution is weighted according to the specific case (accounting for the nanofiller typology, the morphology and the functionalization).

As a first step in this direction the present authors have developed some models to assess nanoparticle debonding stress which accounts for surface stresses and the emergence of an interphase surrounding the nanoparticle with a relevant change in the local elastic properties [64,65]. Indeed, nanoparticle debonding might take an important role not only as mechanism itself, but also as trigger for phenomena like plastic void growth or matrix shear yielding [66,67].

## 5. Conclusions

In the present work the main issues of nanocomposite modelling have been discussed and a description of some modelling strategies available in the literature has been provided. Most of these are micromechanical-based, and should then be updated to include the typical features of the nanoscale.

It has been acknowledged that in the most general case three main stages should be addressed in nanocomposite modelling, and each stage might be tackled with the aid of a dedicated model. Accordingly, the different strategies available in the literature, aimed at predicting the mechanical properties of nanocomposites, have been classified into three groups: Micromechanical, Nanostructural and Molecular, depending on how many and which of the basic models have been used within the strategy. The concept of assembling basic models to build a multiscale modelling strategy has been defined here as "Three Stage Strategy" (TSS).

The most important features of each strategy have been discussed, together with benefits and drawbacks. Significant examples, taken from the literature, have been provided as well.

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