Modeling and simulation techniques for polymer nanoparticle composites – A review

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Abstract
The present review article aims at summarizing some recent advances in modeling polymer nanoparticle composites (PNCs) reinforced with nanoparticles (NPs), having different sizes and shapes. They are added to a polymer matrix (PM) following a given selected fraction (e.g., in terms of volume fraction (VF)). In order to gain a deeper insight to model the mechanical properties of PNCs, the research teams have been modifying the existing micromechanics models (i.e. for two-phased PNCs) and finite element analysis (FEA) for microscale to nanoscale is being used. As a result, new formulations have been incorporated into commercial software packages to predict some properties of PNCs (e.g., elastic properties). Most recently, the modification of these models to three-phased PNCs has also been discussed. Some of the few studies already published on this subject show some difficulty for accurately modeling the interfacial region (IR), also known as interphase, between the matrix and the NPs in the PNCs. However, such studies also show that it is possible to capture some aspects of the real behavior of the PNCs (e.g., tensile modulus). Much more research is needed, so this review article also aims at stimulating further research on this subject.

Keywords:
Polymer–nanoparticle composites
Interphase
Modeling
Finite elements
Elastic properties
Review

1. Introduction
Since the middle of the last century, polymeric matrices (PMs) have been widely used in industry in many applications (surface coatings, adhesives, painting materials, electronic devices, among others) and also as a constituent of polymeric composites (PCs) widely used in automotive, shipbuilding, aerospace and civil construction applications. PMs can be of different chemical types [1–5] and can be divided into thermoset and thermoplastic polymers depending on their internal structure between polymer chains (cross linked networks) [6]. Nowadays, one of the most widely used PM for PCs is the epoxy (EP), a thermosetting material. When any PMs are used as a constituent of the polymeric composites (PCs), they are called the first phase (FP).

Under hard working conditions, PMs must provide good mechanical, thermal and tribological properties in order to ensure good mechanical performances. However, thermosetting PMs have some well-known disadvantages, such as: low flow, poor resistance to crack initiation and propagation (low toughness), brittle failures, high coefficients of linear thermal expansion, among others. For these reasons, in past years, a considerable amount of research effort has been devoted to improve the performance and to solve the disadvantages of PMs. As a consequence, the most common technique is the addition and dispersion of modifiers into the PMs [7]. Several type of modifiers can be used, such as rubbers and fillers/particles, among others [7]. These modifiers are called the second phase (SP) of PCs.

In the last years, some studies have reported the advantages of incorporating into PMs small and rigid inclusions acting like reinforcements, such as fibers and/or micrometer size fillers, with high thermal and mechanical properties. Several reinforcements have been studied, such as silica (SiO2) [8], alumina (Al2O3) [9], titanium (TiO2) [10], graphene [11,12], graphite [13,14], nanoclays [15] and carbon nanotubes [16]. For a given volume fraction (VF) or weight fraction (WF), the incorporation of such reinforcements can substantially improve the toughness, mechanical and thermal properties, as well as optical and electrical (resistivity) properties, wear resistance, gas and liquid barrier, flame retardancy and durability of PMs, when compared with those of the neat PMs [9]. However, such polymer micro particle composites (PMCs) can also exhibit some lower properties (e.g., impact resistance and tensile strength if rigid particles are used) when compared with those of the corresponding neat PM [9]. For this reason, there is a need for a suitable selection of fillers that provide the optimal mechanical properties required for each specific application.
A new approach aiming at overcoming these problems is related to nanotechnology and uses fillers in the nanometer scale (nanoparticles, NPs). Several authors [17–20] have demonstrated the advantages of substituting micrometer size by nanometer size fillers, already available in the market. This improves even more the characteristics of PMs when compared with those of conventional PMCs. Such improvements in polymer nanoparticle composites (PNCs) include an increase in the modulus of elasticity [9,10,21–23], in the strength [9,10,24], in the stiffness, toughness, in the durability, in the electrical conductivity [4,25–27], in the heat resistance/fire retardation [28,29], in the tribological properties [30] and in the biodegradability [31,32], as well as a decrease in the gas permeability [23,33–35] and in the flammability [32,33,36]. These improvements are generally observed in materials with much lower contents of nanofillers, when compared with those of microfillers in conventional PMCs, which might compensate the higher cost of nanofillers [37]. For instance, the relatively low cost of rigid nano alumina particles or nano alumina platelets due to the lower energy demand for production, when compared with other nanofillers (e.g. carbon nanotubes and titanium), makes it able to be used as nanofiller to produce low price PNCs directly applicable in many fields of the industry [9].

Good mechanical improvements of PNCs incorporating such NPs are observed even at very low filler contents [38]. For instance, previous studies reported that the inclusion of 0–10 vol.% of pre-treated nano alumina platelets into EP matrix increased the fracture toughness up to 120% and the tensile modulus up to 50% when compared with the neat PM [9,39]. It was also reported that the inclusion of 10 vol.% of nano alumina spherical particles into epoxy PM can increase the flexural modulus up to 40% and the flexural strength up to 15% when compared with the neat PM [9]. For these reasons, in recent years, PNCs filled with NPs (with size <100 nm [1,40–42]) have gained increasing interest from the research community.

Fig. 1 shows some metallic or nonmetallic oxides (alumina, titanium and silica) widely used as a reinforcement of PNCs.

The higher properties of PNCs are induced by the physical presence of the NPs which process higher characteristic specific surface area (SSA) to volume ratio (i.e. higher surface contact of NPs with PM), which significantly improve their reactivity [43,44], the interaction of the PM with the NPs and also the state of filler dispersion [9,45].

Fig. 2 illustrates the possible commercial shapes of NPs with sizes bellow 100 nm (spherical, cylindrical, ellipsoidal, disc-shaped, cuboid, irregular, thin platelets and nanotube).

It should be noted that some difficulties still exist before PNCs can be used with full confidence in the industry. For instance, the incorporation of NPs into PMs still shows some processing difficulties, such as the formation of particle agglomerates and the non-uniform dispersion. This motivated some research intended to find better techniques of processing the NPs to minimize agglomeration and to ensure better dispersion. Among other techniques, ultrasonication and ball milling have been used with some success [51]. In order to also improve even more the chemical interactions of the NPs with the MPs, the dispersion homogeneity and the mechanical properties of PNCs, recent studies have shown the advantages of using pre-treated (functionalized or coated) NPs at the surface, e.g. with silane-coupling agents, instead of untreated NPs [52]. Some previous articles concluded that the need for more studies still persists, especially involving to carrying out more experimental and mainly theoretical studies on PNCs in order to confirm the influence of several variable studies (type, shape, size and % loading of NPs, among others) as well as also to propose reliable forecasting models to predict the properties of PNCs [32,33,36]. These latter can constitute a successful and cheap option (in comparison with experimental works) to characterize the properties of PNCs. As a consequence, analytical and numerical models able to account for the peculiar physical phenomena related with the inclusion of
NPs into MPs, in order to bridge their effects from the nanoscale to the macroscale size, are still required [53].

The purpose of this review article is to compile the main results of the still few published works which used finite element analysis (FEA) models to predict the elastic properties of PNCs, namely the tensile modulus. In such works, the SP used to reinforce the PMs is constituted by NPs, including silica [18,43,53] or nanoclays [15,39]. Others types of NPs, such as graphene, graphite and carbon nanotubes, are not covered in this review. These fillers have been modeled by different model techniques (some details are given in Section 4) rather than by FEA. Interesting readings are referred to the literature for more details [50,54–66]. This review article also discusses the principal conclusions from the selected research works and aims at encouraging further research in this research field.

The article is organized as follows. In Section 2, the peculiarities of the different phases of the PNCs are summarized. In Section 3, some findings from selected previous studies are presented and summarized. In Section 4, a brief introduction to the continuum methods that are currently employed in PNCs is presented. This comprises: Halpin–Tsai (H–T) model, Mori–Tanaka (M–T) model, equivalent continuum model (ECM), self-consistent model (SCM) and finite element analysis (FEA). Detailed descriptions of each method will not be presented. Section 4 also presents some reasons to justify why this article gave greater importance to previous works that applied FEM to model PNCs. Section 5 summarizes and discusses the positive and negative aspects related with some predictions results obtained by the selected research works. Finally, Section 6 presents the principal conclusions and the closing remarks.

2. Polymer reinforced systems – the third phase (IR)

From a theoretical point of view, two-phase PNCs would not have any priority in comparison with two-phase PMCs, if one considers similar particles shape ratios and VF. However, NPs, if well dispersed in the matrix, offers a higher SSA when compared to...
microparticles. In fact, SSA increases with decreasing particle size \[9,20\]. Consequently, PNCs show large portion of interfacial region (IR) in comparison with PMCs with the same particles VF \[43,44\]. For this reason, PNCs are better characterized by a hierarchical structure, which includes the nano, the micro and the macro length-scales \[53\], being the micro length-scale effect an additional phase: the third phase (TP). In others words, PNCs are actually a three-phase system: PM or matrix (FP) + NPs (SP) + IR (TP).

Fig. 3 shows the different phases that can be considered for the modeling and simulation of PNCs. The effective transport properties are passed hierarchically from the very outside (from the PMs – FP – which has been reported as the unfilled, pristine, neat or control phase, see number 1 in Fig. 3) to the very inside (NPs – SP, see number 2 in Fig. 3) \[39\]. The load transfer take places into the IR (see number 3 in Fig. 3). In some cases, it is also possible to consider interfacial layers, between the NPs and the IR, see number 4 in Fig. 3. Fig. 4 shows a detail of the formation of IR around a microsphere into an EP resin. The thickness of the IR can be approximately 1–2 nm \[43,67,68\].

Experimental observations \[70–73\] and numerical results \[61,66,74–78\] led to the conclusion that the IR presents different properties (physical and mechanical) when compared to those of both the PM and the NPs. The IR is created by interactions which constrain polymer chains around the surface of the NPs \[79\] connected either by covalent bonds \[79,80\] or through van der Waals forces \[81–83\]. These interactions depend on the fillers’ shape, size, surface structure and surface chemistry, as well as on the dispersion quality, adhesion strength quality and IR between NPs and PM \[84–90\].

IR properties play an essential role in the final performance of PNCs \[32,70–73\]. If the adhesion strength quality of the IR is weak, the NPs are unable to carry any part of the external load and may shift and break the initial bonds causing irregularities to PM \[91\]. In that case, the strength of the PC cannot be higher than that of the neat PM. In the other hand, if the adhesion strength quality of the IR is strong enough, the stresses and elastic deformation can be transferred from the PM to the NPs \[92\]. However, if the yield strength of the PNC is higher than that of the neat PM, the effective load and the deformation transfer takes place in the IR \[93\]. This will contribute for the increasing of the aspect ratio (AR) of the NPs, which will enhance the properties of the final PNC \[4,94,95\].

Previous studies \[9,52,89,96\] have demonstrated that the adhesion strength quality of the IR can be improved by a pretreatment or functionalization at the surface of the NP (e.g. with silane groups). Moreover if the NPs are well dispersed into the PM, the IR causes additional fracture mechanisms, which can explain the increase of fracture toughness observed in PNCs.

From the above, it can be stated that the particularities and properties of IR are important aspects to be accounted for the study of PNCs. Nevertheless, the majority of the published studies on PNCs ignore the IR and only consider the properties of the matrix and NPs for NPCs modeling.

So far few studies have directly taken into account the influence of the IR into the PNC properties (mainly by molecular dynamics (MD) and/or analytical methods \[15,61,66,74–78,97\]), nor the influence of NPs spatial distribution and/or clustering of NPs which also constitute important aspects \[6,15,53,98\]. Aiming at accounting for the molecular aspects into continuum-based methods, some authors have included into their micromechanics tools the presence of the IR. Its properties can be computed by mean of MD simulations which provide, as outputs, the radial extension of the IR as well as the elastic properties averaged through the thickness \[18,61,74–76,99–101\]. MD modeling enables the identification of the equivalent continuum model (ECM) in terms of the internal stress field characteristics of the nanofiller and the hosting matrix, as well as the global stiffness of the PNC by computational chemistry methods (Fig. 5) based on quantum chemistry \[101\]. However, the number of these studies is not sufficient to formulate a reliable law of variation of the IR properties across the thickness.
and size [102]. Since MD deals with very specific fields from chemical physics, MD simulations are not addressed in this review work.

Several studies use average values for the Young’s modulus ($E$) and Poisson’s ratio ($ν$) of the PM and NPs to estimate the mechanical properties of the IR [50,63,103]. It should be pointed out that experimental specific techniques (e.g., nanoindentation equipment eventually coupled with Atomic Force Microscopy (AFM)) can also be used to estimate the mechanical characteristics of the IR as well as its average width [72,73,104]. However, such techniques are still not widely used.

The selected research works for this review article [15,18,39,43,53,70] consider the particularities and properties of the IR in PNCs modeling. The elastic mechanical properties of the IR were estimated based on the average property values for PM and NPs. For the selected studies, Table 1 shows an overview of the materials properties, namely $E$ and $ν$, used to characterize the matrix, NPs and IR.

### 3. Previous studies and principal findings

Theoretical models have been extremely useful in predicting the properties of certain PMCs. Micromechanical models have been developed to evaluate elastic properties of PMCs with respect to VF and to the shape of the reinforcing particles [105]. In general, PMCs properties can be predicted by the rule of mixtures (ROM), also known as Voigt–Reuss model [6,42].

For the case of PNCs, the ROM might not be directly applicable because in PNCs the effects of several variables must be considered, such as the NPs shape, size, number and VF, as well as the IR and distribution of NPs into the matrix [6]. PNCs properties are affected not only by direct mechanical effects (e.g., load transfers) but rather by physical and atomistic effects [15]. To evaluate this aspect, models are especially useful for assessing certain parameters and fundamental mechanisms behind mechanical property enhancements of PNCs, namely the variables previously referred as well as the anti-crack effects provided by NPs (which increase toughness) [6,66,106]. For this purpose, further efforts have been devoted in the recent studies to develop numerical approaches able to include the mentioned parameters.

Some recent studies have shown the applicability of FEM for modeling PCs with a nanometric SP and also a TP (IR). More details regarding the choices of the selected research works about FEM and meshing can be found in Section 4.

For instance, Pontefisso et al. [53] developed a new algorithm in a finite element (FE) code, based on the use of the Ripley function...
for the generation of 3-dimensional (3D) representative volume elements (RVE). In this new code, the authors included the IR surrounding the NPs and the NPs were distributed by using a tool, the complete spatial random distribution (CSRD). These authors also analyzed the effect of the material morphology on the overall interphase amount and on the elastic properties of PNCs. In some cases, a computational analysis was also used to study the effect of the IR thickness and its properties on the elastic properties of the PNCs. These authors concluded that, when the IR is softer than the matrix (\( E_I/E_M = 0.5 \), being \( E_I \) the elastic modulus (EM) of the IR and \( E_M \) the EM of the matrix), the reinforcement effect due to the addition of NPs is almost cancelled by the low interphase properties. On the other hand, a stiffer interphase \( (E_I/E_M > 1) \) results in a more pronounced increase of the EM of the PNC. The referred authors also concluded that the increase of the IR thickness gave an enhanced stiffening effect to the PNC.

Mortazavi et al. [43] developed a 3D FEM for the investigation of IR effects on the EM and thermal conductivity (TC) of PNCs filled with randomly oriented or unidirectional NPs. These authors studied the effect of the NPs geometry (from long cylinders to spheres and thin discs), the VF, and particularly the effect of the IR thickness and properties contrast by using the hard-core method to avoid intersection or contact between NPs. Contrast is a parameter to account for the ratio between properties, for instance between size of NPs and their average spacing in the matrix or between elastic properties of IR to the matrix. The authors concluded that, while the IR effect is significant for spherical NPs, it seems to be less effective for other geometries, namely for thin disc shaped or long cylinders NPs. The results also indicate that the increase of interphase to matrix properties contrast leads to higher reinforcement effects due to the inclusion of NPs.

Others authors developed a computational numerical-analytical model for PNCs, taking into account the IR and the particle clustering effect in 2D (e.g., Peng et al. [15]). These authors employed the developed model to analyze the inter-relationships between microstructures and mechanical properties of PNCs. The model was improved by the Mori–Tanaka approach, with the inclusion of the NPs geometry and the clustering. A program code was used by the authors for the automatic generation of 2D multiparticle unit cells (UCs) on the basis of the “grid method” algorithm. This program code was incorporated in a commercial software package. With this model, the authors observed that the EM of the PNCs increased as the aspect ratio of NPs also increased. The authors also observed that the thickness and properties of IR, as well as the shape and degree of NPs clustering have strong influence on the final mechanical properties of PNCs. From their results, the authors concluded that high aspect ratio NPs, such as nanoplatelets and nanotubes, are the most efficient enhancement NPs.

Wang et al. [18] also chose to develop a computational numerical-analytical model with a special program code to study the effective interphase layers around NPs with and without overlapping in 3D multiparticle UCs. In this research work, the effects

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**Table 1**

Materials properties considered in the selected research works.

<table>
<thead>
<tr>
<th>References</th>
<th>Phases</th>
<th>Material system</th>
<th>Matrix (PM) E(GPa)</th>
<th>Nanoparticles (NPs) E(GPa)</th>
<th>Interphase (IR) E(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pontefisso et al. [53]</td>
<td>Filler (spherical silica, radius ( r_0 = 10 ) nm), IR (thickness, ( t ) and matrix (EP resin) Homogeneous and isotropic materials</td>
<td>3 0.35</td>
<td>70</td>
<td>0.17</td>
<td>6</td>
</tr>
<tr>
<td>Mortazavi et al. [43]</td>
<td>Filler (silica, radius ( r_0 = 1 ), IR (covering layer of the outer surface of filler) and matrix (EP resin). Homogeneous and isotropic materials</td>
<td>3.5 0.3</td>
<td>70</td>
<td>0.3</td>
<td>(a) Thickness of 0–0.6 nm</td>
</tr>
<tr>
<td>Peng et al. [15]</td>
<td>Filler (nanoclay, ( r_0 = 1 ) nm), IR (thickness: 1.2 nm) and PM. Isotropic and linear elastic phases; Clusters sizes: 18, 24, 30, 40 and 60 nm</td>
<td>4.2 0.4</td>
<td>88.7</td>
<td>0.26</td>
<td>8.4 (stiff); 4.2 (medium); 3.5 (soft)</td>
</tr>
<tr>
<td>Wang et al. [18]</td>
<td>Matrix (polyimide) + filler (silica) + IR (stiffer (outer layer) and softer (inner layer)); particle radius and IR thickness are constant: 12 Å</td>
<td>4.2 0.4</td>
<td>88.7</td>
<td>0.26</td>
<td>3.5 (functionalized)</td>
</tr>
<tr>
<td>Li et al. [39]</td>
<td>Filler (montmorillonite clay platelets, AR = 100), IR (thickness, 2 nm) and matrix (polyurethane); Low SR (&lt;100) or large SR (up to 10,000); Perfectly bonded, isotropic and elastic phases</td>
<td>0.025 0.48</td>
<td>Range: 0.125, 0.250, 0.500, 2.5, 25, 250</td>
<td>0.375</td>
<td>0.075</td>
</tr>
<tr>
<td>Cannillo et al. [70]</td>
<td>Filler (spherical nanosilica, 100–200 nm), matrix (polyacrylate) with IR</td>
<td>0.265 0.35</td>
<td>80</td>
<td>0.18</td>
<td>40</td>
</tr>
</tbody>
</table>

Notes: (a) The information is not available in the article. (b) The information is not available in the article. However, it is likely that this value could be the average from the matrix and the NPs. The same was assumed by these authors for \( E_i \).

Details about the symbols in the table can be found in the list of symbols.
of the effective IR properties, NPs sizes, shapes (spherical, cylindrical, elliptoidal and disc-shaped) and VF, on the mechanical properties of PNCs, were studied in numerical works. Based on their results and assuming soft IR, the authors concluded that the elastic properties of the PNCs improved with the increasing of the NP size up to 10 nm. For higher sizes, no notable influence was observed. Assuming that the IR would be stiffer than the matrix, the effect of size and shape, and the enhancement efficiencies of three typical inclusions (sphere, fiber-like particle, and platelet) at nanoscale.

In a different way, Li et al. [39] proposed a modification to the hierarchical multi-interphase model (HMM) based on the classical elasticity theory. The HMM can be used to study the influence of the IR on the enhancement mechanism of PCs in the elastic regime, but only for cases in which the stiffness ratio (SR) between the inclusions and the matrix would be lower than 100. For cases with larger SRs (up to 10,000) it would be essential to introduce a morphology parameter into the HMM. The authors developed the modified hierarchical multi-interphase model (MHMM) to predict the effect of size and shape, and the enhancement efficiencies of three typical inclusions (sphere, fiber-like particle and platelet) at nanoscale.

The prediction results, both with HMM and MHMM, showed that NP size-dependency of NPC depends highly on the IR properties and also on the morphology and aspect ratio of the NPs. The critical contribution of IR was explained by relating the IR to the surface-to-volume ratio of the NPs and by the interaction between the inclusion and the matrix through IR. The results have also shown that with the increasing scale of RVE the IR effect would decrease and eventually the properties of NPC would become IR independent at relatively larger scales. The authors also observed that, based on HMM, when compared with fiber-like NPs, platelets showed much better enhancement efficiency.

Almost a decade ago, Cannillo et al. [70] studied the mechanical properties of PNCs and developed a numerical model able to reproduce the peculiar PNCs features, such as the morphology and the characteristics of the NPs. These authors mentioned that their computational approach revealed that a TP, namely the IR, should be taken into account in the model in order to accurately reproduce the obtained experimental results [5]. Although only the most recent literature shows the importance of the IR for the modeling and simulation of PNCs, in 2006 Cannillo et al. [70] already had a futuristic vision and stated this, mostly based on their experimental work. They concluded that the modeling of PNCs can be closer to the complex and heterogeneous behavior of PNCs if the three-phases are considered into the model. These authors obtained the EM of the PNCs evaluated by means of the computational model, starting from the microstructural information obtained by scanning electron microscope (SEM) and the intrinsic constituent’s properties (matrix and particles). In summary, Cannillo et al. [70] also concluded that FEA is effective at the nanoscale to evaluate the overall properties of PNC as a function of microstructural characteristics if the model include the IR around the NPs as a third constituent material. The authors also concluded that a three-phase model having IR characteristics intermediate between the two other constituents (NP and matrix) would be able to capture the peculiar properties of PNC. The authors stated that even if the assumptions of their model needed experimental verification in terms of a more detailed IR characterization, their results gave important indications regarding NPC modeling. Although Cannillo et al. [70] have modeled particles with sizes in the range of 100–200 nm (>100 nm and, therefore, outside the range to be considered NPs as mentioned in the introduction section), the present review article will also include some of the results from the referred authors.

Table 2 presents an overview of the variable studies and their influence on some studied parameters, as well as the methods and predicted properties, for the selected research works that used FEM with open source codes to predict some properties of PNCs. From Table 2 it can be seen that the selected research works include approaches based on various methods, such as:
semi-analytical + FEM, statistical + FEM, FEM + algorithms/codes. They also focused on a particular spatial dimension (2D or 3D), included the 3 phases (matrix + NPs + IR) and predicted properties in function of the variables studied.

4. Modeling and simulation techniques – models and assumptions

When the classical continuum mechanics theory is used, the macro-scale is commonly regarded as an amount of material over which all the values for the mechanical quantities are averaged and representative of the overall material behavior. However, at macro and micro scales, when dealing with PNCs, the nano scale is relevant as well and represents a single UC of those compound-ing the micro-scale system, thus accounting for the material morphology at the nanoscale [53].

Continuum methods that have been used in PNCs include micromechanics models (e.g., Takayanagi’s model) H–T model, M–T model, Modified ROM and Shear Lag models (Cox models), ECM, SCM and FEA [6,107]. ECM and SCM have even been proposed for modeling the mechanical behavior of single-walled carbon nanotubes (SWNT) composite systems. Odegard et al. [108,109] proposed an approach that used ECM for the constitutive modeling of SWNT in a polypathic composite system. However, as mentioned before, carbon nanotubes as fillers is out of the scope of this review. These fillers have been essentially modeled by different model techniques (ECM and SCM).

Micromechanical models, when applied to PNCs, usually consider the following assumptions: both NPs and matrix behave as linearly elastic materials; perfect bonding exists between NPs and the matrix; the NPs are axisymmetric, identical in shape and size and can be described by their AR [66]. Mostly, these micromechanical models fail to accurately capture all properties of PNCs [70] since the enhancement mechanisms become more and more sensitive to the morphology of the NPs [39]. For this reason, some authors violate basic assumptions of the classical composite and modify their micromechanics models to solve such limitations.

For instance, the basic assumption assumed by Pontefisso et al. [53] is the absence of overlapping particles, although the authors recognize that it might happen that some non-overlapping particles are close enough to share part of the interphase. Wang et al. [18] differentiate the properties of the IR for isolated NPs and for NPs forming clusters, because interface/interphase layer would change between NPs if they are located very closely. For this reason, their computational model incorporate a generalized effective interface model. In this way, uniformity assumption is violated in this case. Li et al. [39], for NPs with large SRs (up to 10,000) and large VF assumed inclusions with elliptical shape with induced uniformity of stress and strain fields in the NPs. With this assumption, HMM provides a lower bound for the stiffnesses of NPCs enhanced by non-ellipsoidal NPs with the same aspect ratio. For cases with high SRs and high VF, Li et al. [39] assumed the violation of uniformity. For the IR, the authors assumed a homogenous layer around the NPs with constant thickness. Overlap of IRs is considered if VF is large. This aspect induced the authors to propose the modified HMM.

It has been also shown [15,102] that surface effects, which are dominant at the nanoscale, can be accurately modeled in a continuum framework by an imperfect coherent IR (using the spring layer model [110]), which includes thick IR and their effects on PNCs properties. For instance, the variation of the mechanical properties of PNCs can be predicted as a function of NP sizes, VF, molecular structure and density of the atoms, through IR thickness [61]. For this, analytical models, semi-analytical models,

| Table 3 |

An overview of the assumed meshing parameters in the selected research works in the field of PNCs modeling.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Meshing parameters</th>
<th>Analyses</th>
<th>Fraction of NPs</th>
<th>Nodes</th>
<th>BC</th>
<th>Loading, BC</th>
<th>Loading, Uniform displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pontefisso et al. [53]</td>
<td>RVEs as function of: IR thickness, VF and spherical NPs random distribution; CSM (modified and unmodified); Unstructured tetrahedral mesh; cubic array of 8 particles</td>
<td>VF varied from 0 to 7.5 (0, 2.5, 5.0 and 7.5 vol. (%))</td>
<td>10-node tetrahedral elements (SOLID 187 in Ansys)</td>
<td>BC – a zero normal average stress</td>
<td>(a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mortazavi et al. [43]</td>
<td>RVEs filled with randomly and oriented NPs; RVE size adjusted by geometry, VF and number of perfect NPs; geometry of NPs was defined by their AR; Interphase thickness defined with respect of NPs radius</td>
<td>Varied from 0 to 10 vol. (%) (0, 2, 4, 6, 8 and 10)</td>
<td>4-node linear tetrahedron shape elements</td>
<td>Perfect BC between NPs, interphase and matrix</td>
<td>Small uniform displacement on one surface (along z-direction) and the others surfaces were fixed only in their normal directions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peng et al. [15]</td>
<td>NPs generated with “grid based algorithm”; IR added as layers of a given thickness surrounding each NP with regular distribution, uniform distribution and random distribution (RSA algorithm)</td>
<td>VF varied from 0% to 10% (0.1, 0.5, 1, 2.5 and 10 vol.%)</td>
<td>4-node plane strain elements and 3-node plane strain elements (CPE3)</td>
<td>Symmetric and perfect BC</td>
<td>Uniform displacements were applied to the right edges of the cells, tensile loading</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang et al. [18]</td>
<td>UC with randomly arranged NPs with different shapes (cylinders, discs, ellipsoids and spheres) and orientations (random and aligned, RSA algorithm)</td>
<td>Varied from 0.1–6 vol. %; fraction for each phase: 5% (particle) and 35% (interphase) and 60% (matrix)</td>
<td>3D 8-node linear brick, C3D9R (single-NP) and 3D 4-node linear tetrahedral elements, C3D4 (multi-NP)</td>
<td>(a)</td>
<td>UCs subject to a uniaxial tensile displacement loading along Y axis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al. [39]</td>
<td>6 RVEs with prismatic shape and thickness of 1 mm and AR = 100</td>
<td>2.5, 5.0 and 10.0 vol.% for NPs; 5.15, 10.3 and 20.6 vol.% for interphase</td>
<td>1–2.5% by weight</td>
<td>3D periodic BC</td>
<td>Displacements in the 1 direction, uni-axial tension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cannillo et al. [70]</td>
<td>Meshes for all microstructural details (i.e., inclusions size, shape, spatial positioning and exact amount); linear elastic properties for fillers and matrix</td>
<td></td>
<td></td>
<td>Perfect BC</td>
<td>Tensile load with plane stress hypothesis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: (a) The information is not available in the article.
Details about the symbols in the table can be found in the list of symbols.
computational methods or statistical continuum methods are required and some attempts have been made to apply the existing analytical micromechanical models for PMCs, for instance: H–T and M–T models, 2D or 3D FEM, statistical continuum theory (SCT) of weak-contrast or strong contrast, and computational models to PNCs (with three-phases) [15,18,39,43,53] (see Tables 1–3). Such attempts are usually performed by using algorithms or codes to include the effective IR effects and the effect of NP shapes, orientations, distributions, clustering and IR overlapping.

Based in the current knowledge, Fig. 5 shows a schematic representation of the principal steps concerning the modeling of PNCs with three-phases and includes two different paths (see the bold lines). The two paths, one concerning the micromechanical models and another one concerning the FEM, can merge because, in the case of PNCs modeling, it is necessary to join other methods to FEM to solve some existing limitations related with the description of the overall composite behavior (matrix + nanofiller + interphase). Fig. 5 can obviously be adapted and other steps can be added as the knowledge about PNCs modeling will be developed in the future.

4.1. Finite element method (FEM)

The FEM is a general numerical method and a versatile tool for the modeling and simulation of a wide range of engineering problems. With FEM it is possible to obtain approximate solutions in space to initial-value and boundary-value problems, including time-dependent processes. The entire domain of interest is spatially discretized into an assembly of simply shaped subdomains (e.g., hexahedra or tetrahedral (3D) and rectangles or triangles (2D)) without gaps and without overlaps. The subdomains are interconnected at joints (i.e., nodes). The computational limitations and modeling complexities of FEM can impose limits on the maximum number of elements but enables the consideration of complex and nonlinear constitutive relationships into the analysis. FEM has been incorporated in many commercial software packages (e.g., ABAQUS, ANSYS, Palmyra and OOF) [66].

FEM have been also used for modeling TC, EM, stiffness and viscoelastic properties of PNCs with low NPs content [15,18,39,43,53,98]. The results of these studies show that FEM is mainly suitable for a particular type of inclusion geometry. Furthermore, the inclusions should be of uniform size and distributed uniformly in the matrix. In a real PC, the reinforcements are of varying size and geometry, distributed randomly in position and orientation. Moreover, local agglomerations or stacking of the reinforcements can occur especially in the case of nanometer size reinforcements. Thus, the real microstructures of PNCs are very complex. For this reasons, the interrelationships between microstructures and the overall properties of PNCs may not be captured effectively by analytical models. Instead, these interrelationships can be analyzed with the use of discretized numerical models, which incorporate discrete, real or generic microstructures of materials and also incorporate deformation and damage characteristics, particularly on a local scale [6,66].

In the case of PNCs, a very challenging work is the simulation of the mechanisms responsible for the strong effect of small amount of NPs on the extraordinary properties of PNCs. Also quite challenging is the generalization of the micromechanical methods of modeling common microscale reinforced composites in the case of nanoscale reinforcement with the incorporation of the IR [18].

4.2. Simulation techniques

The effects of different reinforcing parameters have been studied in literature using simulation techniques. From the macroscale to the microscale, the concept of “material point” is substituted by the representative volume element (RVE), taken as sufficiently small to be mathematically regarded as an infinitesimal volume of the macroscale [53]. Many simulations investigate the local continuum properties through analysis of RVE. RVE has to be, by definition, large enough to be statistically representative of the smallest UC that can be used to simplify the entire composite system, i.e., RVE has to describe the properties of the overall composite system (EP + NP + IR) built with the real material microconstituents and microstructures, to ensure the length scale and the first-order effect on the macroscopic behavior [46,66]. Fig. 6 illustrates the various types of UCs which can be selected from a typical PNC with two-phases. For three-phases PNCs, it is necessary to take into account that an interfacial layer (IR) will surround each particle represented in Fig. 6.

RVE was proposed by Nemat-Nasser and Hori [111] and has been used in a repeating or periodic nature in the full-scale model. Whole composite materials can be represented as a periodic array of RVEs, accounting for the IR effect, random orientation and distribution of the filler, discontinuities and coupled mechanical and non-mechanical properties [66,70].

An essential step into the analysis of the effect of the filler distribution on the PNCs elastic properties is the choice of appropriate boundary conditions (BCs) to be applied to the RVE. This topic has been widely debated in the literature and several BCs have been proposed through the years. Dirichlet BC (uniform displacement), Neumann BC (uniform tension), mixed BC and periodic boundary conditions (PBCs) [53,112–114] have been applied to the RVE. It is known that Dirichlet and Neumann BCs provide the upper (Voigt) and lower (Reuss) bounds of the solution, respectively, while the PBCs provides intermediate estimates [113,114]. For this reason, Kari et al. [115] stated that PBCs must be applied to the RVE models. This implies that each RVE in the composite has the same deformation mode and there is no separation or overlap between the neighboring RVEs after deformation. However, from the results given by Terada et al. [113] it was also evident that for VF <10% (the typical% loading range of the selected research works in Tables 1–3 and in literature) the effects of BCs on the elastic properties are very limited [53].

In the case of PNCs, their complexity and irregularity needs a special attention with respect to the optimal choice of RVE and generation of unit cell models (UCMs). UCMs have limitations when the reinforcements are of assorted size and randomly distributed (clustering effect) and oriented [103].

In FEM, one should verify the dependency of the reported results to the RVE size. The size of RVE naturally correlates to
the number and geometry of the considered particles. For spherical inclusions, the RVE size is only dependent on the number of spheres and VF as well. For cylindrical and platelet inclusions, by increasing the VF and AR of the NPs, one must also check that the RVE size must be higher than the maximum dimension of the NPs [116].
Table 3 shows an overview of the meshing parameters adopted by the selected research works from Tables 1 and 2, in the field of PNCs modeling. Table 3 shows the type of analysis, the variables under analysis (NPs size, shape and spatial positioning), fraction of NPs (VF, WF, SR or AR), nodes, bounding conditions and applied load.

The general results from the selected research works in Table 3 show that, with the right choices, it is possible to set up a reliable model, which could be used as a predictive tool to estimate the properties of PNCs systems. However, new developments still are needed to reach a sufficiently refined model for the description of the interphase (IR). Instead of a homogeneous region with uniform properties throughout its thickness, IR can be treated as a layer with graded properties, with values ranging between those of the PM and those of the NPs [70]. This approach would lead to a more realistic simulation of the overall PNC behavior and, thus, to more accurate results.

5. Obtained results from the selecte studies and discussion

As mentioned before, so far few studies developed FEM models for PNCs taking into account the three-phases (matrix + NPs + IR) and used them to evaluate the PNCs properties (e.g., [15,18,43,53,70]). Most of these studies have only focused the estimation of the EM of PNCs by FEM. More recently, Mortazavi et al. [43] evaluated the EM and TC of PNCs by FEM. Most of the referred studies present the normalized elastic modulus (Ei/Em) as a function of the VF of the NPs for different interphase properties (Ei/Em) or interphase thickness.

Fig. 7 represents graphically the predicted normalized elastic modulus (Ei/Em) as a function of the volume fraction of the NPs, for different interphase properties (Ei/Em) and for some of the previously referred studies [15,18,43,53]. If the overall Young's modulus was given by the authors, the conversion to obtain the normalized elastic modulus was performed. Ei is the overall EM of the composite, Em is the EM of the interphase and Em is the EM of the matrix.

In particular, Fig. 7 shows:

- from Pontefisso et al. [53]: the effect of the interphase to the matrix elastic properties ratio, Ei/Em (0.5, 1, 2 and 4), for a constant interphase thickness (t = 5 nm) and for different VFs (0%, 2.5%, 5% and 7.5%) of spherical NPs;
- from Mortazavi et al. [43]: the effect of the interphase to the matrix properties contrast (LMC: 0, 0.5, 0.75, 2 and 3) for a constant interphase thickness (0.5 nm), for low filler to matrix properties contrast of 20 and for different VFs (0%, 2%, 4%, 6%, 8% and 10%) on normalized Ei/Em for spherical NPs;
- from Peng et al. [15]: the effect of the interphase properties (with 1 or 3 layers and different EM) on the normalized Ei/Em for spherical NPs and for different VFs (0%, 2%, 4%, 6%, 8% and 10%); and
- from Wang et al. [18]: the effect of the interphase properties (stiffer or softer) on the NPs Young's modulus for spherical reinforcements and for different VFs (0.1–6%).

Fig. 8 shows that when the interphase is softer than the matrix (Ei/Em = 0.5, see Section 3), no reinforcement effect due to the addition of NPs exists. On the other hand, a stiffer interphase (Ei/Em > 1) results in a strong increase of the normalized Ei/Em for the PNCs [43,53]. From Peng et al. results [15] it is possible to observe small differences between 3-layer (3L) and 1-layer (1L) effective interphase models for the case of soft effective interphase (1L3.5GPa, 3L3.5GPa, 1L4.2GPa and 3L4.2GPa). However, for stiff effective interphase (1L8.4GPa and 3L8.4GPa) the normalized Ei/Em is stronger for 1L than for 3L. Normalized Ei/Em is stronger for the case of the stiff effective interphase (1L8.4GPa and 3L8.4GPa), but rather smaller for the soft effective interphase (e.g., 1L3.5GPa and 3L3.5GPa).

For all studies presented in Fig. 7, results show that the increase in normalized Ei/Em values strongly depends on the interphase properties, namely the effect of the IR to the matrix elastic properties ratio or contrast. Stiffer IR results in higher values for Ei/Em. For PNCs with stiffer IR, the stiffness of the PNCs generally increases as the particle VF increases and the relationships between the normalized Ei/Em and the nanoparticle VF are nearly linear.

Fig. 8 represents graphically the normalized elastic modulus (Ei/Em) as a function of the VFs of the nanoparticles, for different interphase thicknesses and for the same previously referred studies [15,18,43,53].

In particular, Fig. 8 shows:

- from Pontefisso et al. and Mortazavi et al. [43,53]: the effects of the interphase thickness (Ei/Em = 2 or at constant interphase properties contrast of 2) for different interphase thicknesses (0, 0.5, 0.75 and 1 nm or 0, 0.2, 0.4 and 0.6 nm, respectively) on the Ei/Em of PNCs;
- from Peng et al. [15]: the effect of the interphase thickness (0, 0.6, 1.2 and 1.8 nm) with a constant interfacial layer (1.2 nm) on the Ei/Em of PNCs for different VFs (0.1%, 0.5%, 1%, 2%, 5% and 10%).

Fig. 8 shows that the increase of the interphase thickness provides an enhanced stiffening effect [43,53]. From Mortazavi et al. [43] results it is possible to observe that by increasing the interphase thickness, Ei/Em increases by a power of about three. However, from Peng et al. [15] results the opposite happens. Ei/Em of PNCs decreases with the increasing of effective interphase thickness. This can be due to the inclusion of a interfacial layer with 1.2 nm into the model, as referred by the authors.

The results form Mortazavi et al. and Pontefisso et al. [43,53] (Fig. 8), and also from other authors [1,39,117,118], clearly show the importance of the inclusion of the interphase properties and size into the modeling of PNCs for the correct assessment of the mechanical properties of PNCs.

It should be noted that Figs. 7 and 8 seem to show very large variations. This occurs because the results from the different selected studies were condensed in the same graphs. From Tables 1–3 it can be seen that the PNCs simulated by the authors as well as the used models have noticable differences (NPs properties, matrices properties, IR properties, used software packages; basic assumptions for the numerical models, meshing parameters and different condition loading). For this reason, the results from different studies cannot be directly compared with each other. However, from Figs. 7 and 8 general tendencies can be drawn with respect to the evolution of the normalized elastic modulus with respect to the VF of the NPs and some interphase properties. It should also be noted that the results presented in Figs. 7 and 8 are numerical previsions for the normalized elastic modulus of PNCs obtained by the selected authors, as function of the VF of the NPs and different IR properties, namely the IR to the matrix elastic properties ratio (or contrast) and the thickness of IR. No experimental results on these IR properties with similar NPs were found in literature, so no experimental and reliable data exists to be directly compared with the numerical results of Figs. 7 and 8. The actual elastic properties of IR, as well as the actual thickness of IR, are not given in a reliable way in experimental studies, which is understandable since such properties are not easy to be experimentally obtained. However, from previous review articles on experimental studies (e.g., [9,10]), some general conclusions can also be drawn from the results presented in Figs. 7 and 8.
In general, it is experimentally observed that, for similar rigid NPs as those simulated by the studies from Figs. 7 and 8, the normalized elastic modulus (or the tensile modulus) of the PNCs tends to increase almost linearly with VF (it should be pointed that the majority of the experimental studies present results until 5 vol.%) [9,10]. The results of the simulations presented in Figs. 7 and 8 reflect this actual behavior and seem to indicate that actually the IR is stiffer compared with the matrix in the tested PNCs for which such tendency is observed. Experimental results also show that pre-treated NPs generally provides higher normalized elastic modulus (or tensile modulus) for the PNCs, for the same VF and for similar rigid NPs as the ones simulated by the selected studies (Figs. 7 and 8). Coated NPs develops stronger IR in PNCs and should provide IR with higher thicknesses. The results of the simulations presented in Figs. 7 and 8 generally indicate that the normalized elastic modulus increases with the increasing of the thickness of IR. This seems to agree with the trends that are observed in tests.

From the previous points of view, the results of the simulations presented in Figs. 7 and 8 seems to capture the actual behavior experimentally observed.

Others important conclusions from studies whose results are not shown graphically in the present section can also be stated. From Li et al. research [39], intrinsic consistency was verified by FEM simulations and for composites with larger values of SR (100–10,000). The enhancement efficiency of the NPs becomes very sensitive to the morphology of the filler. A comparison of the predicted results from the HMM and the 3D FE simulations showed that for the cases with low SR (<100, range 1), the HMM can accurately predict the enhancement efficiency of the composite, which increases slowly with a nonlinearly behavior. For the cases with large SR (100–10,000, range 2), the HMM predict the enhancement efficiency of the composite in the following way: the initial increment of the enhancement efficiency is fast but for larger SR the increment slows down and the enhancement efficiency approaches its asymptotic limit. It is observed that the enhancement efficiency could not go further, no matter how large the SR is. The accuracy of the HMM decreases with the increase of the VF and SR. FEM for PNCs needs to cover the Range 2 and that can be possible with MHMM, when the VF and/or the SRs are high. One important feature of the HMM and the MHMM is their particle size-dependency.

Fig. 8. Normalized elastic modulus ($E_c/E_m$) as a function of the VFs of the NPs and interphase thicknesses [15,18,43,53].
From Canillo et al. results [70], it is possible to observe that the modeling results were significantly lower than the experimental ones [5] for the functionalized NPs. However, for unmodified NPs it was observed that the predicted values were close to the experimental ones, although the computational results were slightly greater. Cannillo et al. [70] also obtained estimations from the EM of the PNCs from analytical equations (H–T [119]) widely adopted by Lewis–Nielsen (L–N [94]) for PMCs. The results show that the predicted properties (EM), obtained both from the numerical model and from the analytical equations, were related to composites with silica inclusions of micrometric scale and without functionalization. For this reason, the authors included the interphase layer as a third phase in the model and obtained computational results very close to the experimental data. Canillo et al. [70] concluded that, if the model would include an interphase layer, the applicability of the FEM, even at the nanoscale, would be effective to evaluate the overall properties as a function of the microstructural characteristics.

Li et al. [39] and Canillo et al. [70] did not present the normalized elastic modulus ($E_i/E_m$) as a function of the VF of the NPs for different interphase properties (including IR thickness $E_i/E_m$), nor the overall Young's modulus as a function of the VF of PNCs. So, the results from these studies were not shown graphically in Figs. 7 and 8.

The results of the selected research works [15,18,39,43,53,70] could be useful to guide the design of PNCs materials and to prove the substantial effect of the interphase zone, surrounding the nanofiller (randomly oriented or unidirectional), on the mechanical properties (e.g., elastic properties) of PNCs, with respect to the PM. Others effects, such as the filler geometry (long cylinders to sphere, ellipsoidal and disc-shaped), VF, particle clustering effects with or without overlapping, are issues which need to be considered at nano-scale, in order to better reproduce the peculiar PNCs features by numerical modeling. The referred research works have also considered these effects and their most important conclusions are summarized in the next section.

6. Conclusions and closing remarks

This article has presented a review of modeling and simulation techniques for predicting the properties of PNCs, filled with NPs (e.g., silica and nanoclays). Despite the number of studies on modeling PNCs properties is still limited, some important conclusions can be drawn from this revision work, namely:

- Predictions of three-phase models considering matrix (PM) + NPs + IR are usually more in agreement with experimental results than those of two phase models (matrix + NPs). This shows the importance of the IR and its contribution in the properties improvement of PNCs;
- PNCs multiscale homogenization approaches were used based on continuum mechanics principles and can be categorized into the following four classes: micromechanics models, ECM, self-consistent model and FEA;
- New formulations (FEM + modified micromechanical models, FEM + functions, FEM + algorithms, etc.) can be incorporated into commercial software packages and open source codes and be used in simulations with PNCs with three phases to predict their properties;
- New formulations are possible to be derived with the incorporation of the IR properties and the morphology of the NPs. These two parameters (IR and morphology of the NPs) are crucial to predict the mechanical improvement of PNCs with an accurate modeling approach;
- In the computational grids, the IR should be inserted as a third phase (TP), i.e., a layer (or several sublayers) surrounding the NPs (taking into account if the NPs are or not considered as functionalized NPs or unmodified NPs);
- As the NPs geometry deviates slightly from the spherical shape, the NPs properties present considerably higher reinforcement effects;
- The interphase presents the maximum effect for spherical NPs and the minimum effect for disc shaped NPs;
- The EM of PNCs increases with the increasing of the AR, thickness and shape of the NPs and also with the increasing of the degree of particles clustering;
- The effect of the VF of NPs on the mechanical properties of PNCs is determined by the IR properties. While the stiffness of the PNC increases with increasing particle VF for the stiff IR, the effect is inverse for soft IR;
- HMM is accurate for the cases with low SR (less than 100). For the cases with high VF and/or high SR, modifications are need due to the non-uniformity of the stress strain fields in the inclusions (MHMM);
- In general, and with respect to the normalized elastic modulus (or tensile modulus) of PNCs, the comparison of the results from numerical simulations with experimentally observed trends seems to indicate that the numerical models that better capture the actual behavior of PNCs with rigid NPs are those that incorporate IR with higher stiffness compared to the matrix and IR with adequate thicknesses if coated NPs are used.

As the scale decreases, the inclusion morphology becomes more and more important with respect to the enhancement efficiency and should be considered in the PNCs design. However, the development of an effective numerical modeling approach to predict their properties based on their complex multiphase and multiscale structure is still at an early stage. Modeling of PNCs properties is a complicated task due to the number and arrangements of the reinforcing phases that need to be considered, as well as the shapes, orientations and spatial distributions of NPs. Global PNCs models that can be applied to the most general cases and that would consider the variation of such parameters are yet to be developed. More numerical studies are also needed to enable the bounds or limitations to be fixed for the NP properties. Such developments of the numerical models would give more reliable predictions.

New concepts, theories and computational tools should be developed in the future to turn the PNCs modeling and their simulations technique increasingly closer to reality.

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References