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Effectiveness of the random sequential absorption algorithm in the analysis of volume elements with nanoplatelets

Alessandro Pontefisso [a], Michele Zappalorto [b,*], Marino Quaresimin [b]

[a] Department of Wind Energy, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, Building 228, 4000 Roskilde, Denmark
[b] Department of Management and Engineering, University of Padova, Stradella S. Nicola, 3, 36100 Vicenza, Italy

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ABSTRACT

In this work, a study of the Random Sequential Absorption (RSA) algorithm in the generation of nanoplatelet Volume Elements (VEs) is carried out. The effect of the algorithm input parameters on the reinforcement distribution is studied through the implementation of statistical tools, showing that the platelet distribution is systematically affected by these parameters. The consequence is that a parametric analysis of the VE input parameters may be biased by hidden differences in the filler distribution. The same statistical tools used in the analysis are implemented in a modified RSA algorithm to overcome this issue.

1. Introduction

In the past decades polymer nanocomposites surprised the scientific community with outstanding improvements of polymer functional [1,2] and mechanical [3,4] properties. Nowadays thousands of scientific publications per year testify the huge interest in this research area.

Several materials have been created and tested using different types of nanoreinforcements, which can be classified as a function of their geometry: spherical (e.g. alumina nanoparticles), rod-like (e.g. CNTs) and platelet-like (e.g. nanoclays). Focussing on nanoplatelets, many authors showed their capability in increasing the matrix tensile properties [5], fracture toughness [6], barrier [7] and antibacterial properties [8]. However the same authors presented also the complexity involved in processing these materials and the need of better understanding their behaviour in order to employ them effectively [9].

The modelling of polymer nanocomposites has proved to be challenging: the continuum mechanics hypotheses are questionable at the nanoscale, and the filler–matrix chemical interactions strongly affect the nanocomposite mechanical properties [10–12]. In order to account for these features, some authors introduced filler–matrix interfacial properties [13] while others an interphase layer, meant as a third phase between the filler and the matrix, with peculiar properties different from those of the composite constituents [14–19]. Regardless the implemented approach, the determination of the interfacial/interphase properties is still an area of active research and tools such as Molecular Dynamics [20] or inverse modelling with experimental data best-fitting on micro-mechanical models [21] are being used.

Several research papers were published on the computational modelling of nanoplatelet reinforced composites [22–24] in an attempt to shed light onto the mechanisms involved in these materials. Ma et al. [22] proposed a FE simulation of nanoclay–epoxy nanocomposites to study their impact behaviour. In particular they implemented a Random Sequential Absorption (RSA) algorithm to create 2D Volume Elements (VEs) of the material and to analyse their damage processes taking into account the reinforcement–matrix traction–separation law. Hbaieb et al. [23] modelled the stiffness of polymer/clay nanocomposites. They created 2D and 3D VEs with aligned and randomly oriented platelets, through a RSA algorithm, and performed a comparison with the Mori-Tanaka model. Dai and Mishnaevsky [24] studied the damage evolution in a nanoclay reinforced epoxy. They created 2D and 3D VEs of aligned or randomly oriented platelets, obtained with a RSA algorithm, and performed XFEM simulations of the initiation and propagation of the damage.

The above mentioned papers reported a non-negligible effect of the filler orientation and distribution on the overall mechanical properties, highlighting the importance of the nanocomposite morphology when modelling these materials. Another element which

* Corresponding author.
E-mail address: michele.zappalorto@unipd.it (M. Zappalorto).

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emerges is that the RSA algorithm is the most common approach in nanoplatelet VE generation. This is reasonably due to the easiness of its implementation and the soundness of its statistical base. However, when dealing with nanoplatelets, the randomness inherently possessed by the RSA algorithm is biased, as found by Cricrì et al. [25] while studying the stiffness of nanocomposite materials using a periodic 3D-FEM model. After obtaining statistical parameters of the reinforcement orientation through TEM analyses of the material, they implemented a RSA algorithm able to take into account those parameters in the construction of 3D models. In their analyses, they highlighted the link between the VE size (in terms of number of platelets) and the possibility for it to exhibit isotropic structural characteristics. In doing so, they remarked the connection existing between the input parameters for the VE generation and the reinforcement distribution resulting from the RSA algorithm.

In the present work, three statistical indexes are proposed with the aim to study the platelet distribution within VEs. Then a RSA algorithm is implemented to generate VEs of different aspect ratios, filler volume fraction and number of platelets, proving the existence of a systematic effect of the input parameters on these VEs. Finally a way to overcome this issue when using RSA approaches is proposed, as well.

2. Statistical tools

2.1. Preliminary remarks on the platelet shape

In the literature several nanoplatelet shapes can be found, also depending on the material and the manufacturing process. Within this context, worth of being mentioned is the paper by West et al. [26] who documented that kaolinite platelets often exhibit an euhedral six-sided shape. Santos et al. [27] reported several micrographic images proving that, while varying the manufacturing process, the shape of bohemite platelets can be hexagonal, euhedral, ellipsoidal or rhomboidal whereas Ci et al. [28] presented an innovative cutting technique for Graphene platelets along crystallographic orientations, which allows shapes with corner angles multiple of 60° (i.e. triangles, rhombi, hexagons, etc.) to be obtained.

Starting from these experimental evidences, in this paper the hexagonal platelet shape is employed for the analysis, this choice offering a physical relevance to the research, beyond the considerations specifically aimed at the RSA approach.

2.2. Analysis of the platelet orientation distribution

The platelet distribution is defined in terms of centre positions and platelet orientations. Considering that in this study hexagonal platelets have been used, the platelet shape results in a quasi-transversal-isotropic behaviour, allowing the use of the sole unit vector orthogonal to the platelet plane, $\vec{n}$, as orientation descriptor. In fact, if the shape possesses an approximate radial symmetry, its orientation can be described by the sole direction of its axis: in this case the orientation in the plane is disregarded, but the approximation introduced is a minor one. With these hypotheses, the shape aspect ratio (intended as the ratio between its planar dimension and its thickness) is deemed enough to characterize the influence of the planar dimension on the overall reinforcement distribution. The parameter $\vec{n}$ is studied within the frame of the statistical analysis of axial data through the definition of an orientation matrix $[T]$ [29–32]. Expressing, for each platelet i, $\vec{n}$ as $\vec{n}_i = \langle x_i, y_i, z_i \rangle$, $[T]$ is evaluated as:

$$[T] = \begin{bmatrix} \sum_i x_i^2 & \sum_i x_i y_i & \sum_i x_i z_i \\ \sum_i x_i y_i & \sum_i y_i^2 & \sum_i y_i z_i \\ \sum_i x_i z_i & \sum_i y_i z_i & \sum_i z_i^2 \end{bmatrix} \tag{1}$$

Fig. 1 gives a representation of $\vec{n}_i$ while other examples of this approach can be found in [33–35]. Solving the eigen-problem associated to $[T]$ it is possible to obtain 3 eigenvalues and 3 eigenvectors which give information about the preferred orientation of $\vec{n}_i$ within the VE. Eigenvalues have been defined as υ_1, υ_2, υ_3 with $\upsilon_1 \geqslant \upsilon_2 \geqslant \upsilon_3$.

To evaluate the effects of the input parameters on the VE filler configuration an isotropic distribution of platelet orientations is taken as reference. This assumption gives the upper limit of the υ_3/υ_1 ratio: a value of one means uniform distribution, while decreasing values identify a higher anisotropy. Within this context it is worth of being mentioned the paper by Woodcock and Naylor [30], where it is reported that, in the case of a Complete Random Distribution (CRD), the value expected for υ_3/υ_1 is about 0.67.

The second eigenvalue, as explained in [29], takes part in the definition of a *shape parameter* for the distribution, while the first and the third one are enough to describe a *strength parameter*: the former is useful in discriminating girdle-type distributions from clustered ones, but it is the latter that describes "how far" is the distribution from an isotropic one. Therefore, for brevity and considering that the focus of the analysis is in this last concept, in the following study the second eigenvalue was disregarded.

Alongside the analysis by means of eigenvalues, a qualitative analysis of the distribution was carried out by means of a graphical representation of $\vec{n}_i$. The tip of each unit vector can be plotted as a point on a sphere of radius 1, assuming a common origin for each vector (Fig. 2a). Considering that in the case of platelets $\vec{n}_i \equiv -\vec{n}_i$ (i.e. the sign of the vector magnitude is irrelevant) all data have

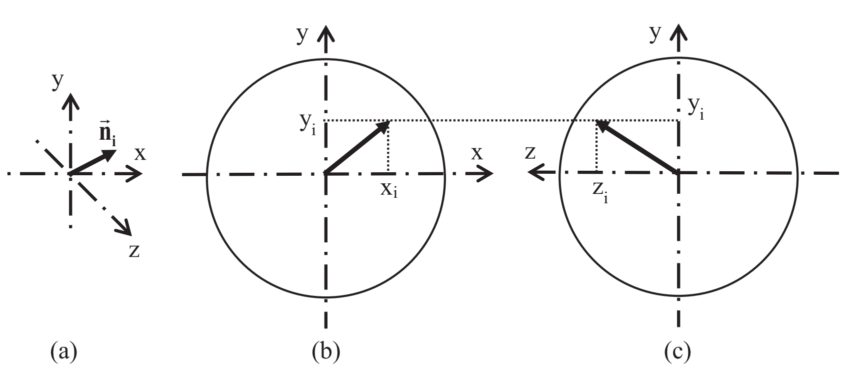

Fig. 1. The spatial unit vector $\vec{n}_i$ (a) and its projection on plane x–y (b) and z–y (c). These projections allow the evaluation of the unit vector components x_i, y_i and z_i.