Computational Materials Science 82 (2014) 122–130

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Numerical and analytical modeling of the stiffness of Polymer–Clay Nanocomposites with aligned particles: One- and two-step methods

M. Pahlavanpour [a], P. Hubert [b], M. Lévesque [a,*]

[a] Laboratory for Multiscale Mechanics (LM2), CREPEC, Mechanical Engineering Department, École Polytechnique de Montréal, Montreal, Canada
[b] Mechanical Engineering Department, McGill University, Montreal, Canada

ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form 13 September 2013
Accepted 16 September 2013
Available online 18 October 2013

Keywords:
Homogenization
Finite element
RVE
Nanoclay
Interphase

ABSTRACT

This paper studies one- and two-step homogenization models for predicting the stiffness of Polymer–Clay Nanocomposites (PCN) with aligned particles. In particular, the influence of the Effective Particle (EP) concept central to two-step models is assessed for numerical as well as analytical modeling. This study covers intercalated PCN, as well as exfoliated morphologies in the presence of interphase. The predictions of analytical and simplified numerical homogenization models were compared against detailed 3D Finite Element (FE) simulations where the PCN layered microstructure is explicitly simulated. The Representative Volume Element (RVE) was rigorously determined. The theoretical predictions were also compared against experimental data extracted from the literature. It was found that both numerical and analytical two-step methods may significantly diverge from the FE simulations of the detailed microstructures. In general, the analytical multi-coated inclusions model delivers more reliable results than two-step methods. Despite their higher computational costs, one-step FE models are necessary, depending on the PCN microstructure and the desired accuracy. It was also found that the more the EP is different from the nanoclay, in terms of rigidity and aspect ratio, or the higher the volume fraction is, the more the accuracy of two-step numerical models is deteriorated.

1. Introduction

Polymer–Clay Nanocomposites (PCN) are used in various sectors like packaging, transportation and construction. Clays, in their natural form, are stacks of parallel nanoclay platelets. Depending on the degree of separation and polymer penetration between the nanoclays, three different morphologies for clay–polymer systems can be found: intercalated, exfoliated and aggregates. Exfoliated morphology occurs when completely separated single nanoclays are dispersed in the polymer matrix. The intercalated morphology results from the penetration of polymer chains between parallel nanoclays. At the molecular level, the interactions at the interface between the nanoclay and the polymer matrix result in the formation of an interphase with a thickness of a few nm.

Numerous studies have been devoted to the mechanical behavior prediction of intercalated and exfoliated PCN [1–7]. However, only a limited number of such studies have taken into account the interphase effects [2,4,5]. Analytical studies can be generally categorized in one- and two-step homogenization models. Two-step models rely on the *Effective Particle* concept [1,2] as a first homogenization step. This concept homogenizes the multiphase layered particle (the exfoliated nanoclay surrounded by the interphase or the intercalated stacks) into a single phase, the Effective Particle (EP). The second step then computes the overall properties of the simplified two-phase composite (i.e. distributed EPs in a uniform matrix). The EP concept has simplified the homogenization problem but its accuracy has not been rigorously evaluated, yet. One-step models have been mostly applied to exfoliated PCN, with or without incorporating the interphase [4,5]. However, to the authors' best knowledge, no one-step study has been performed for intercalated composites. More importantly, no comparative studies have been performed to assess the range of validity and time-efficiency of two- and one-step models.

The numerical modeling of PCN has also been the subject of numerous works. The developed models range from simplified 2D [2–4,6] to more complex 3D Finite Element (FE) models [6,7]. In most of the numerical works, the representativeness of the analyzed models was not verified, which can raise questions about the accuracy of the reference data used for the comparisons. The EP concept has been also used in numerical models [2–4,8]. Figiel et al. [3] examined the EP concept in a 2D FE study by comparing the predictions of their model constituted of EPs against those of detailed layered microstructures. They have shown that the concept could lead to accurate predictions, provided that the anisotropy of the EPs was taken into account. However, no accurate numerical study has yet dealt with the 3D explicit representation of the different phases.

* Corresponding author. Tel.: +1 514 340 4711x4857; fax: +1 514 340 5264.
E-mail address: martin.levesque@polymtl.ca (M. Lévesque).

0927-0256/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.commatsci.2013.09.038

The purpose of this work was to study further the relevance and accuracy of the EP concept in two-step numerical, as well as analytical, modeling. Two analytical one-step models have been adopted to predict elastic properties of PCN. The predictions of analytical homogenization models were compared to 3D FE simulations of PCN detailed microstructures for intercalated and exfoliated microstructures. The effect of the interphase was explicitly incorporated in numerical as well as in analytical modeling. The originality of the present work lies in the fact that the Representative Volume Element (RVE) was rigorously established and that neither analytical nor numerical models were limited by simplifying assumptions such as isotropic particles and the EP concept. To the best of the authors' knowledge, their 3D FE models in which the interface is explicitly represented are the most representative FE model published so far for the studied microstructures. Furthermore, numerical results were compared to experimental data extracted from the literature for exfoliated Nylon-6/Montmorillonite (MMT) and intercalated MXD6 Nylon/MMT nanocomposites.

The paper is organized as follows: Section 2 presents a brief background on PCN and the modeling methods. Section 3 discusses the proposed modeling strategy. The properties of the constituent phases for the studied PCN are presented in Section 4. Section 5 presents the performance evaluation of the various models by comparing their predictions against benchmark numerical and experimental data published in the literature. Finally, Section 6 concludes this work.

2. Background

2.1. Polymer–Clay Nanocomposites

Nanoclay platelets have a thickness of about 1 nm and their lateral dimensions may vary from 30 nm to several microns [9]. In an exfoliated morphology, an interphase region forms around each nanoclay platelet (Fig. 1(a)). Interphase forms under two circumstances; changes in crystallinity for semicrystalline polymers and immobilization of polymer chains adjacent to nanoclays for all polymers. In this work, the thickness of the interphase was considered as negligible in intercalated morphologies, especially for amorphous polymers, when compared to that of the intercalated stack [4,10]. In an intercalated morphology, an interlayer space, called *gallery*, separates the nanoclays. The distance between the central planes of two consecutive nanoclays is denoted by $d_{(001)}$ (Fig. 1(b)).

2.2. Two-step homogenization models

Two-step models based on the EP concept were initially developed for intercalated PCN [1,2]. They were later used for exfoliated nanoclays with interphase [8]. For the intercalated morphology, the EPs were mechanically equivalent to layered reinforcing stacks consisting of nanoclays and galleries (Fig. 1(b)). For exfoliated morphologies, given the small nanoclay thickness, it was assumed that the interphase lied only on the top and bottom faces of the nanoclay, leading to a three-layer reinforcing stack (Fig. 1(a)).

2.2.1. First step

In the works of Mesbah et al. [4] and Pahlavanpour et al. [8], the properties of the EPs were computed as per the modified rule of mixtures [11] as:

$$E_{p,11} = E_{p,33} = \chi E_s + (1-\chi)E_t, \quad (1)$$

$$\nu_{p,12} = \nu_{p,32} = \chi \nu_t + (1-\chi)\nu_s, \quad (2)$$

$$E_{p,22} = \frac{E_s E_t}{\chi E_t + (1-\chi)E_s - \chi(1-\chi)\beta E_t E_s}, \quad (3)$$

$$\nu_{p,13} = \frac{\chi \nu_s E_s (1-\nu_t^2) + (1-\chi)\nu_t E_t (1-\nu_s^2)}{\chi E_s (1-\nu_t^2) + (1-\chi)\nu_t E_t (1-\nu_s^2)}, \quad (4)$$

$$G_{p,12} = G_{p,32} = \frac{G_s G_t}{\chi G_t + (1-\chi)G_s - \chi(1-\chi)\eta G_t G_s}, \quad (5)$$

$$G_{p,13} = \frac{E_{p,11}}{2(1+\nu_{p,13})}, \quad (6)$$

where E, ν and G denote the Young's modulus, the Poisson's ratio and the shear modulus, respectively. Subscripts 1, 2 and 3 correspond to the Cartesian coordinate axes shown in Fig. 1 (i.e. the platelets have their thickness along axis 2). Subscripts s, p and t refer to the nanoclay, the EP and the third phase (interphase in the exfoliated or gallery in the intercalated morphology), respectively. β and η were defined as:

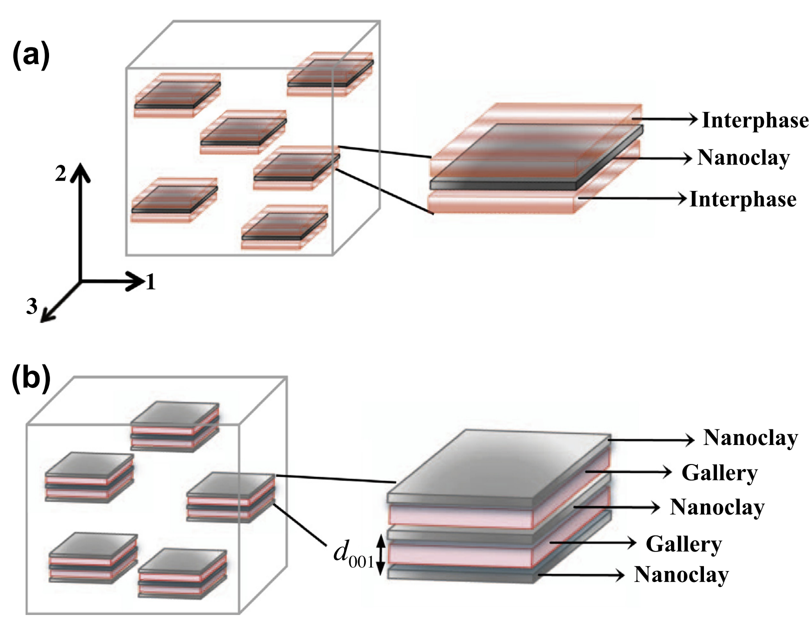

Fig. 1. Layered structure of reinforcing stacks in (a) exfoliated PCN and (b) intercalated PCN. The interphase is not considered for the intercalated morphology.