Micromechanics-based constitutive modeling of plastic yielding and damage mechanisms in polymer–clay nanocomposites: Application to polyamide-6 and polypropylene-based nanocomposites

A. Mesbah [a,b,c], F. Zaïri [a,b,*], M. Naït-Abdelaziz [a,b], J.M. Gloaguen [a,d], K. Anoukou [a,b], A. Zaoui [a,e], Z. Qu [a,b], T. Boukharouba [c], J.M. Lefebvre [a,d]

[a] Univ Lille Nord de France, F-59000 Lille, France
[b] Université Lille 1 Sciences et Technologies, Laboratoire de Mécanique de Lille (LML), UMR CNRS 8107, F-59650 Villeneuve d'Ascq, France
[c] Laboratoire de Mécanique Avancée, USTHB, BP32 El-Alia Bab-Ezzouar, 16111 Alger, Algeria
[d] Université Lille 1 Sciences et Technologies, Unité Matériaux Et Transformations (UMET), UMR CNRS 8207, F-59650 Villeneuve d'Ascq, France
[e] Université Lille 1 Sciences et Technologies, Laboratoire Génie Civil et géoEnvironnement (LGCgE), EA 4515, F-59650 Villeneuve d'Ascq, France

ARTICLE INFO

ABSTRACT

The present work focuses on the continuum-based micromechanical modeling of the elastic–plastic stress–strain response including damage mechanisms of polymer–clay nanocomposites. The micromechanical elastic–plastic-damage model includes both the actual microstructure of the said composites using a multi-scale approach and the microstructural evolution related to damage accumulation under applied macroscopic deformation. The interfacial debonding between clay nanoparticles and polymer matrix, and the polymer matrix voiding are the two prevalent damage events considered. The tensile stress–strain response and micromechanical deformation processes of polyamide-6 and polypropylene-based systems reinforced with modified montmorillonite clay at various concentrations are experimentally investigated by a video-controlled technique. The usual shear yielding deformation mode of neat polyamide-6 is altered by the presence of clay platelets which induce a dilatational process due to interfacial debonding. In addition to matrix shear yielding, a dual-dilatational deformation mechanism by crazing and interfacial debonding is revealed in polypropylene–clay nanocomposites. Using the intrinsic deformation micromechanisms and elastic–plastic properties of the polymer matrix, and the nanocomposite structural characteristics, the micromechanical model is found to successfully describe the experimental results of the two nanocomposite materials in terms of tensile stress–strain response and inelastic volumetric strain.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Since the first works published by the Toyota group [1,2], polymer–clay nanocomposites have received considerable scientific and industrial attention in recent years. Over the past decade, a large number of works [3–13] dealt with the continuum-based micromechanical modeling of their effective elastic stiffness, but very few works [14,15] focused on their effective plastic yielding. To predict the effective elastic–plastic response of polymer–clay nanocomposites, Zaïri et al. [15] recently proposed a micromechanical model integrating the effects of size and clay structural

parameters, i.e. number of clay layers, interlayer spacing and clay layer dimensions. The aim of this paper is to extend the latter micromechanical model by taking into consideration the effect of local damage in the deformation process, such as the crazing in the polymer matrix and the debonding along the interface between the polymer matrix and nanoparticles. As revealed in the few experimental reports available in the literature [16–20], these deformation mechanisms can progressively accumulate in polymer–clay nanocomposites, and have an important effect on the macroscopic response. Experiments on polyamide-6 and polypropylene-based nanocomposites with different clay loadings were also achieved in this paper to characterize the role of polymer matrix and clay content on the micromechanical deformation processes and the elastic–plastic response. The microstructural changes involved during deformation was determined on the basis of a videoextensometry method able to control the local true axial

---

* Corresponding author at: Université Lille 1 Sciences et Technologies, Laboratoire de Mécanique de Lille (LML), UMR CNRS 8107, F-59650 Villeneuve d'Ascq, France. Tel.: +33 328767460; fax: +33 328767301.
   E-mail address: fahmi.zairi@polytech-lille.fr (F. Zaïri).

strain rate. The choice of polyamide-6 and polypropylene as matrix of nanocomposites offers an interesting validation of the micromechanical model as the first one deforms exclusively by shear yielding and the other exhibits both shear yielding and crazing, the supplementary voiding being a consequence of the clay incorporation, i.e. nanoparticle-matrix debonding.

The paper is organized as follows. Section 2 is devoted to the description of the micromechanics-based constitutive equations. Section 3 presents the experiments and the model-experiments comparisons. Concluding remarks are given in Section 4.

2. Micromechanics-based constitutive equations

This section presents constitutive equations based upon the continuum-based micromechanical framework to predict the effective elastic–plastic response of polymer–clay nanocomposites[1]. Polymer–clay nanocomposites are treated as an Eshelby-type inclusion problem in which the representative volume element consists in randomly oriented discrete elastic isotropic spheroids (i.e. the clay particles) randomly dispersed in a continuous elastic–plastic isotropic medium (i.e. the polymer matrix).

2.1. Effective elastic–plastic response of polymer–clay nanocomposites

In this subsection, the shear yielding in the ductile polymer matrix, occurring without volume change because of purely deviatoric nature, is supposed to be the only deformation mechanism and the constituents are assumed to be perfectly bonded at interfaces. Several experiments reported in the literature evidenced that the clay-polymer interactions provoke the perturbation of the local structure and dynamics of the polymer matrix e.g. [1,21,22], thus resulting in a part of polymer around clay nanoparticles (i.e. the so-called interphase) which has neither the properties of the polymer matrix nor those of the clay nanoparticles. Let us consider a three-phase nanocomposite consisting of a polymer matrix (phase *M*, with stiffness tensor $\mathbf{C}^M$ and volume fraction ϕ^M), clay nanoparticles (phase *P*, with stiffness tensor $\mathbf{C}^P$ and volume fraction ϕ^P) and interphase (phase *I*, with stiffness tensor $\mathbf{C}^I$ and volume fraction ϕ^I)[2]. The effective elastic stiffness tensor $\overline{\mathbf{C}}$ of the nanocomposite is given by [23]:

$$\overline{\mathbf{C}} = \mathbf{C}^M \cdot \left\{ \mathbf{I} - (\mathbf{T}^P + \mathbf{T}^I) \cdot [(\mathbf{S}^P \cdot \mathbf{T}^P + \mathbf{S}^I \cdot \mathbf{T}^I) + \mathbf{I}]^{-1} \right\} \quad (1)$$

in which $\mathbf{T}^P$ and $\mathbf{T}^I$ are two fourth-order tensors expressed as:

$$\mathbf{T}^P = -\phi^P \left[\mathbf{S}^P + (\mathbf{C}^P - \mathbf{C}^M)^{-1} \cdot \mathbf{C}^M \right]^{-1} \text{ and }$$

$$\mathbf{T}^I = -\phi^I \left[\mathbf{S}^I + (\mathbf{C}^I - \mathbf{C}^M)^{-1} \cdot \mathbf{C}^M \right]^{-1} \quad (2)$$

Note that the Liu and Sun [23] formulation contains a minor misprint which was corrected. The terms $\mathbf{S}^P$ and $\mathbf{S}^I$ denote the Eshelby tensors for the nanoparticles and the interphase, respectively.

In order to predict the effective mechanical response of nanocomposites containing randomly oriented nanoparticles, the averaging procedure over all possible orientations is performed. The size effect of nanoparticles is explicitly incorporated in the micromechanical model by considering the interphase thickness e_I as a characteristic length scale [10,11,15]. The intercalated morphology of nanocomposites is also taken into consideration using a

multi-scale approach starting from the nanostructure and allowing relating the nanostructure to the effective mechanical response. In this approach, the intercalated nanoparticle, seen as a laminated composite consisting of several clay layers separated by polymer, is replaced by an equivalent homogeneous nanoparticle but having transversely isotropic properties [15]. By designating the 1-direction as axisymmetric axis and the plane 2–3 to be the transversely isotropic plane, the effective stiffness tensor of the equivalent homogeneous nanoparticle $\mathbf{C}^P$ can be given, by means of the engineering matrix form, by:

$$\left[C_{ij}^P\right]_{6\times6} = \begin{bmatrix} \lambda_{11,P}+2\mu_{11,P} & \mu_{12,P} & \mu_{12,P} & 0 & 0 & 0 \\ \mu_{12,P} & \lambda_{22,P}+2\mu_{22,P} & \mu_{23,P} & 0 & 0 & 0 \\ \mu_{12,P} & \mu_{23,P} & \lambda_{22,P}+2\mu_{22,P} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu_{23,P} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu_{13,P} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu_{13,P} \end{bmatrix} \quad (3)$$

where $\mu_{ij,P}$ and $\lambda_{ij,P}$ are the effective Lame's constants of the homogeneous nanoparticle expressed as functions of the Lame's constants of the gallery (i.e. the polymer matrix in the interlayer spacing) and the clay, both assumed isotropic:

$$C_{ijkl}^{gallery} = \lambda_G \delta_{ij}\delta_{kl} + \mu_G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \text{ and }$$

$$C_{ijkl}^{clay} = \lambda_C \delta_{ij}\delta_{kl} + \mu_C(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \quad (4)$$

Where δ_{ij} signifies the Kronecker delta.

The Lame's constants of the gallery are assumed to be the same as those of the matrix, $\lambda_G = \lambda_M$ and $\mu_G = \mu_M$.

The aspect ratio of the equivalent nanoparticle α is given by:

$$\alpha = \frac{(N-1)d_{001} + t_C}{L_C} \quad (5)$$

where N is the number of clay layers in the nanoparticle, d_{001} is the interlayer spacing, t_C is the clay layer thickness and L_C is the clay layer length.

Because the characteristics of nanocomposites are known in terms of clay weight fraction, it is necessary to express the nanoparticle volume fraction ϕ^P as a function of the clay weight fraction W^C using the following relationship:

$$\phi^P \approx \frac{\rho_M}{\rho_C \phi^{C/P}} W^C \quad (6)$$

where ρ_M and ρ_C are the matrix and clay densities, respectively, and $\phi^{C/P}$ is the proportion of clay in the equivalent nanoparticle:

$$\phi^{C/P} = \frac{Nt_C}{(N-1)d_{001} + t_C} \quad (7)$$

The effective plastic yielding of nanocomposites is considered from the continuum plasticity theory. The von Mises yield criterion with isotropic plastic hardening is assumed for the polymer matrix. The effective yield surface[3] $\overline{F}$ is expressed as a function of the effective stress $\overline{\boldsymbol{\sigma}}$ and the effective equivalent plastic strain $\overline{e}^p$ as follows [24]:

$$\overline{F} = (1 - \phi^P - \phi^I)^2 \overline{\boldsymbol{\sigma}} : \left(\mathbf{P}^{\mathrm{T}} \cdot \mathbf{B} \cdot \mathbf{P}\right) : \overline{\boldsymbol{\sigma}} - \frac{2}{3}\left[\sigma_y + h(\overline{e}^p)^q\right]^2 \leqslant 0 \quad (8)$$

in which σ_y is the initial matrix yield stress, the terms h and q denote the hardening parameters of the polymer matrix, and, $\mathbf{P}$ and $\mathbf{B}$ are two fourth-order tensors, respectively, written as follows:

---

[1] In the text, tensor notation is used where tensors are denoted by bold-face letters. The double dot ":" signifies the tensor contraction between a fourth-order tensor and a second-order tensor, while the single dot "." denotes the tensor multiplication between two fourth-order tensors.

[2] Each constitutive phase is supposed to be an isotropic and homogeneous medium. The intercalated cluster of clay, replaced by an equivalent particle, is considered to be a homogeneous medium but anisotropic.

[3] It was observed in [23,25,26] that the effective yield surface of nanocomposites given by the formula (8) does not strictly obey to the von Mises criterion but is hydrostatic pressure-dependent. This is due to the presence of nanoparticles since the plastic yielding in the polymer matrix is controlled by the von Mises yield criterion.