A MICROMECHANICAL MODEL FOR THE EFFECTIVE VISCOELASTIC RESPONSE OF SEMI-CRYSTALLINE POLYMER-CLAY NANOCOMPOSITES

Kokou Anoukou[*], Fahmi Zaïri[*a)], Gregory Stoclet[**], Moussa Naït-Abdelaziz[*], Ali Zaoui[***], Jean-Michel Gloaguen[**] & Jean-Marc Lefebvre[**]

[*]*Université Lille 1 Sciences et Technologies, Laboratoire de Mécanique de Lille (LML), UMR CNRS 8107, avenue Paul Langevin, F-59650 Villeneuve d'Ascq, France*

[**]*Université Lille 1 Sciences et Technologies, Unité Matériaux Et Transformations (UMET), UMR CNRS 8207, F-59650 Villeneuve d'Ascq, France*

[***]*Université Lille 1 Sciences et Technologies, Laboratoire de Génie Civil et géo-Environnement (LGCgE), EA 4515, F-59650 Villeneuve d'Ascq, France*

Summary The present work addresses the question of the micromechanics-based prediction of the structure-stiffness relationship of semi-crystalline polymer-clay nanocomposites. A self-consistent scheme based on the double-inclusion model is adopted to take into account, in addition to the clay structural parameters, the contribution of matrix crystalline phases in the stiffening. To illustrate the capabilities of the proposed micromechanical model, comparisons with the viscoelastic response of polyamide-6-based nanocomposite systems are presented.

INTRODUCTION

Polymer-based nanocomposites have developed rapidly over the last two decades due to their highly specific mechanical properties compared to conventional polymer-based microcomposites [1]. Among this recent class of materials, the most intensive researches are focused on polymer-based nanocomposites reinforced with inorganic clay, and especially on their synthesis and characterization. Over the past ten years, several authors used approaches issued from the continuum-based micromechanical framework to predict the effective mechanical response of polymer-clay nanocomposites [2-5]. The main result of these investigations is the demonstration that micromechanical models can provide accurate predictions of the effective elastic properties of such materials so long as the morphology is accounted for. However, the applicability of micromechanical modeling techniques was discussed in these works using models considering the heterogeneities diluted in the matrix. Therefore, according to the strong local interactions in nanocomposites acting between particles and matrix but also between particles themselves, the relevance of comparisons between such models and experimental data must be carefully analyzed. In the same manner, the indirect quantitative characterization of the nanocomposite morphology using macroscopic experimental data with such models may be questionable. More recently, Anoukou et al. [6-7] demonstrated the relevance of a micromechanics-based approach using a self-consistent scheme to predict the effective elastic stiffness of polymer-clay nanocomposites. In particular, the effective role of interactions in the stiffening of nanocomposites was emphasized. Although the clay structural parameters were taken into account, the heterogeneous nature of semi-crystalline polymer matrices was completely disregarded in the analyses. In the meantime, several experiments reported in the literature using calorimetry, X-ray diffraction and RMN evidenced that, when clay is added, the crystalline structure of the polymer matrix can be modified. Consequently, a reliable prediction of the structure-property relationship in semi-crystalline polymer-clay nanocomposites using the micromechanical approach requires taking into account explicitly the matrix crystalline structure.

In the present work, the micromechanics-based model presented by Anoukou et al. [6-7] is applied to formulate the effective viscoelastic response of semi-crystalline polymer-clay nanocomposites by taking into account the presence of the crystalline phases of the matrix. To verify the capabilities of the present model, the predictions are compared with the viscoelastic response of polymer-clay nanocomposites made with a semi-crystalline polyamide-6 matrix.

EXPERIMENTS

Polyamide-6-clay nanocomposites with different cooling histories were investigated by Differential Scanning Calorimetry (DSC) and X-ray diffraction in order to examine the crystalline structure. Owing to specific interactions between the amine end groups and the clay surface, the most stable monoclinic α-form is found inhibited and the less stable monoclinic γ-form is formed by default. As direct inputs in the micromechanical model, the relative amount of α- and γ-crystal fractions and their characteristic lengths were quantified. The clay structural parameters were estimated by X-ray diffraction and transmission electron microscopy (TEM). The viscoelastic (glassy to rubbery) response of neat polyamide-6 and its clay nanocomposites was investigated by Dynamic Mechanical Thermo-Analysis (DMTA) under tensile mode.

[a)] Corresponding author. Email: fahmi.zairi@polytech-lille.fr

MICROMECHANICAL MODEL

Let us start by considering a multiphase composite consisting of a linearly elastic isotropic matrix (to which we confer the subscript 0) and, randomly oriented and located, linearly elastic isotropic inclusions (to which we confer the subscripts 1 to n). Considering the double-inclusion model using the consistency condition, in which the infinite reference medium is the composite material itself, the effective elastic stiffness tensor $\mathbf{C}$ of the multiphase composite is given by [8]:

$$\mathbf{C} = \mathbf{C}_0 + \sum_{i=1}^{n} f_i \left(\mathbf{C}_i - \mathbf{C}_0\right) : \mathbf{A}_i$$

where f_i (i = 1,..., n) is the volume fraction of each inclusion i and $\mathbf{A}_i$ is the strain concentration tensor defined as:

$$\mathbf{A}_i = \mathbf{I} + \mathbf{S}_i : \left[(\mathbf{C} - \mathbf{C}_i)^{-1} : \mathbf{C} - \mathbf{S}_i \right]^{-1}$$

in which $\mathbf{S}_i$ is the Eshelby tensor of each inclusion i and $\mathbf{I}$ signifies the identity tensor.

After a series of lengthy but straightforward manipulations, the effective elastic stiffness tensor $\mathbf{C}$ of the multiphase composite may be expressed in terms of the effective bulk and shear moduli, κ and μ, via a system of implicit equations which can be solved simultaneously [6-7]:

$$\kappa = \kappa_0 + \sum_{i=1}^{n} \frac{f_i}{3} \Phi_i \quad \text{and} \quad \mu = \mu_0 + \sum_{i=1}^{n} \frac{f_i}{2} \Psi_i$$

where Φ_i and Ψ_i are scalars expressed in terms of components of the Eshelby tensor $\mathbf{S}_i$ and the elastic constants of the composite (κ and μ), the matrix material (κ_0 and μ_0) and the inclusion i (κ_i and μ_i).

To characterize the structure of studied nanocomposites, three inclusions are considered: the nanoparticles, and the α- and γ-crystal phases. The elastic stiffness tensors of α- and γ-crystal phases as calculated by molecular dynamic simulations by Tashiro and Hiroyuki [9] are used. A particular attention is paid on the decomposition of the monoclinic stiffness tensors of crystals using the Walpole algebra in order to avoid the cumbersome iterative tensorial resolution required by the self-consistent scheme. The nanoparticle structural parameters (i.e. number of clay layers in the nanoparticle and interlayer spacing) are taken into account according to an equivalent stiffness method in which the clay stacks are replaced by homogeneous nanoparticles with predetermined equivalent anisotropic stiffness [6]. The elastic-viscoelastic correspondence principle [10] is applied to the developed micromechanical model in order to predict the effective viscoelastic response.

For the studied nanocomposite systems, the developed micromechanical model provides reasonable predictions of the experimental data. The possible effect of reduced chain segment mobility near the organic-inorganic interfaces, generally associated with the presence of the γ-crystalline structure, is discussed with respect to a hierarchical version of the micromechanical model (i.e. nanoparticle coated by γ-crystalline phase).

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