MODELLING MORPHOLOGY EVOLUTION DURING QUASI SOLID-STATE PROCESSING OF CLAY/POLYMER NANOCOMPOSITES

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1 Introduction

A new family of composite materials is that of polymer nanocomposites, where the filler has at least one dimension at the nanometer length scale. These nanocomposites exhibit some promising potential for improving mechanical and/or barrier properties that can be obtained at low filler loadings. The layered silicate (clay)/polymer nanocomposites have been the most extensively investigated because of their application potential (in e.g. packaging or automobile industry) at relatively low production cost.

Depending on the polymer and organosilicate thermodynamic compatibility, intercalation kinetics and the processing conditions, the nanocomposites can have different morphologies - i.e. they can take the form of polymer reinforced by tactoids (unseparated silicate sheets), intercalated silicate sheets or exfoliated nanoparticles. It is well known that these processing-induced morphologies have different impact on final properties (e.g. mechanical) of nanocomposites. However, it is still unclear what the influence of those morphologies is on end-product properties, as they evolve during quasi-solid state processing (e.g. injection stretch-blow molding). This aspect must be explored to take a full benefit of extraordinary characteristics of polymer nanocomposites. The task is complex, because it involves a relationship between variables of material composition and processing and end-product properties. The authors believe the complexity involved can be handled by exploitation of advanced numerical modelling of the material.

The present work forms part of a wider study, aiming to model the effects of quasi-solid state process conditions on particle structure, dispersion and orientation, and hence on important physical properties of the polymer nanocomposites following processing. This paper focuses specifically on the finite element modelling of the morphology effects on the large deformation behaviour of a layered clay polyethyleneterephthalate (PET) nanocomposite subjected to quasi-solid state processing conditions.

2 Nanocomposite model

The problem is tackled at the material length scale, where one can distinguish single silicate particles embedded in the polymer matrix. It permits accounting for several geometry parameters such as single silicate aspect ratio and orientation, or gallery thickness. Moreover, by this different degrees of intercalation/exfoliation or orientation (from aligned to random) and thereby morphologies can be described. An appropriate representative volume element (RVE) of the nanocomposite is chosen to render it feasible. For the purpose of this work it is assumed that the continuum mechanics theory holds down to the single silicate sheet material length scale. In that respect, we are following the concept reported in e.g. [1]. Thus, most of the molecular features are represented in an average sense. In particular, single silicate sheet properties are obtained by adopting molecular dynamics simulation results in the same way as reported in [1]. The chemical bonding between the single silicate sheet and the matrix is represented in terms of the perfectly bonded interface. The matrix material (PET) behaviour is represented in terms of a physically-based glass-rubber constitutive model proposed by Buckley and coworkers [2]. Regarding the fact that the current study is concerned with temperatures above the glass transition of PET, the bond-stretching part (incorporating intra-/intermolecular interactions) of the model is neglected and only the conformational part (incorporating elastic network with entanglement slippage) governs the polymer deformation under

processing conditions of interest. Matrix model parameters are obtained by fitting them to experimental results obtained from mechanical tests on PET in the processing range of temperature and strain rate. The nanocomposite model is implemented into the commercial FEM-based software ABAQUS. At present, a 2D model under plane strain conditions has been considered. Thus, the silicate sheets and the matrix are discretised using second-order plane strain elements. The PET constitutive model is implemented using the UMAT subroutine of ABAQUS. Periodic boundary conditions are imposed on the nanocomposite RVE.

3 Some results and discussion

Results shown below reveal the effects of the clay aspect ratio, intercalation/exfoliation and orientation in the temperature range (just above the glass transition, at $T \sim 95^o$-100°), where the PET behaves as a rubbery elastic network, and viscous effects associated with entanglement slippage are neglected. In these simulations the PET is assumed to be homogeneous, i.e. its properties remain unmodified. An RVE used in the simulations is shown in Fig. 1, where clay particles (of volume fraction around 5%) are arranged in a columnar manner. Three geometrical parameters are varied – silicate aspect ratio (L/d_s), intergallery/silicate thickness (d_{001}/d_s) and silicate orientation (ϕ) with respect to the load direction.
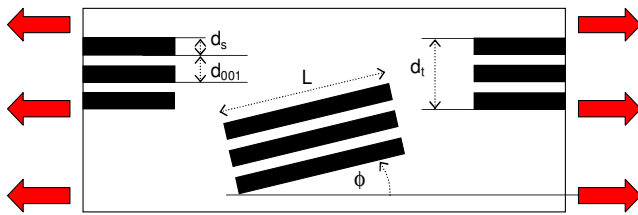

Fig. 1. RVE

Simulated uniaxial true stress-strain curves for three different aspect ratios are shown in Fig. 2 for a fully aligned ($\phi=0$) and exfoliated state ($d_{001}/d_s \rightarrow \infty$). As expected, strong polymer reinforcement by silicate particles is observed as the aspect ratio increases. Thus, the aspect ratio is an important factor that controls nanocomposite deformation, provided that silicate is evenly distributed and fully exfoliated.

Similarly, as the intergallery/silicate thickness ratio decreases ($d_{001}/d_s \rightarrow 1$ and $\phi=0$) the overall true stresses decrease, because of the decreasing shear stress transfer between the particles and matrix (matrix straining between particles decreases). In

addition, the silicate sheets form an intercalated particle as the ratio decreases, thus the bending ability of a single silicate sheet decreases.
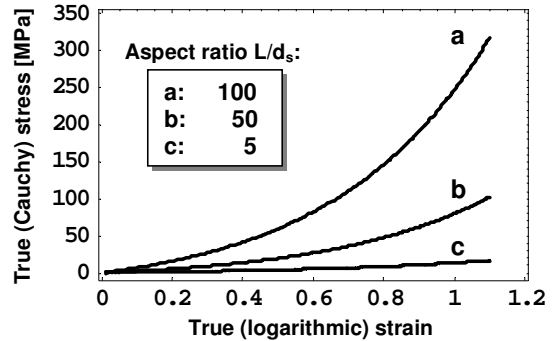

Fig. 2. Aspect ratio effects on stress-strain curves

As the silicate sheets become misaligned with respect to the loading direction, the overall true stresses decrease as compared with fully aligned particle configuration. Moreover, as the RVE elongation increases, the particles start to rotate/bend and tend to align along the loading direction. Depending on the initial orientation (ϕ) and exfoliation degree (d_{001}/d_s), the process can lead to a development of new morphologies. In particular, the particles can undergo further exfoliation, as their orientation increases and initial exfoliation degree is large. It is because of spatial restrictions between silicate sheets are reduced and the shear stresses within the matrix, between silicate sheets, are maximized at the same time. However, above certain particle orientation, no further exfoliation occurs (under applied uniaxial load), because the silicate sheets become more susceptible to debonding.

One of the main problems that have been encountered so far in this work is large distortion of finite elements at applied true strains above 100% leading to simulation termination. This is a serious limitation when one needs to simulate multiaxial deformations experienced during quasi-static solid state processing (~400%). The adaptive meshing seems to be the only remedy and the work on this is ongoing.

References

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