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MICRO-MECHANICAL MODELLING OF SMALL AND LARGE STRAIN BEHAVIOUR OF PARTICULATE NANOCOMPOSITES

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ABSTRACT

This work presents experimental results and micro-mechanical modelling of the small and large strain behaviour of particulate nanocomposites consisting of a soft polymeric matrix filled with rigid submicronic (either PS or silica) inclusions. The small strain properties appeared to be governed by filler-filler interactions as soon as a percolating filler network is developed (> 20%). To account for these observations, a discrete simulation which takes into account the nature of contact between reinforcing particles has been developed. However, the large strain properties can be correctly modelled by means of homogenisation techniques, suggesting that the filler network is broken very soon.

INTRODUCTION

Nanocomposite materials consist of a nanometer-scale phase in combination with another phase acting as a matrix. Work about polymer nanocomposites has exploded over the last few years. Their properties are reported to be different from that of their micro-scale counterparts^{1,2}. These unusual properties may be a consequence of (i) the extremely high interfacial specific area which can reach 100-1000 m²/g and (ii) the very short average distance between reinforcing fillers (about 10⁻⁸ m), down to a value comparable with the macromolecule coils. This can favor the short-distance filler-filler interactions leading, above a critical volume, to the formation of a network (percolation). Though significant progress has been made in developing nanocomposites with different polymer matrices, a general understanding has yet to emerge. A major challenge to further development of nanocomposites is the development of specific micro-mechanical models.

NANOCOMPOSITE SYSTEMS

Different nanocomposites model systems consisting, at room temperature, of a soft polymeric matrix filled with randomly dispersed rigid spherical submicronic particles were processed by mixing a film forming matrix (either poly(butyl acrylate) or poly(styrene-butyl acrylate)) latex and a non film forming filler (either PS or silica) latex. Films were thus processed with a filler ratio varying from 0 to 45% vol. and variable filler-filler interactions.

SMALL STRAIN PROPERTIES: A DISCRETE NUMERICAL APPROACH

The viscoelastic behaviour has been characterized (i) after film formation at room temperature (these PS-PBA and silica-PBA films are referred to as "as dried" films) and (ii) after an annealing treatment performed at 140°C during 4 hours to enhance the interactions between neighboring PS particles by coalescence (these PS-PBA films are referred to as "annealed" films). In all systems, the diameter of filler particles is around 110 nm. Dynamic mechanical analysis of the samples have been performed in torsion in the temperature range [-170; 150 °C] with a heating rate of 1°C/min at a fixed frequency of 1 Hz. From the comparison between the elastic properties of the various systems, the small strain properties appeared to be governed by the filler ratio and by the short range filler-filler interactions as soon as a percolating filler network is developed (> 20%): when the strength of the filler-filler interactions increases, the composite modulus increases.

As an illustration, **Fig. 1** shows the temperature dependence of the real shear modulus of the various nanocomposites containing 25% vol. of filler and the pure PBA matrix: above the PBA main relaxation, the silica-filled nanocomposite displays a higher modulus than that filled with PS (in the “as dried” state). This can be attributed to the presence of hydrogen bonds assumed to take place between silica particles, instead of Van der Waals bonds in the case of PS. Moreover, the relaxed modulus of the PS-PBA nanocomposite having undergone an annealing treatment to induce the coalescence between neighbouring PS particles, is higher than the moduli of as dried PS-PBA and silica-PBA nanocomposites. Thus, these experimental results feature the major influence of the nature of interactions between fillers on the linear mechanical behaviour, above the geometrical percolation threshold.

In that case, classical homogenisation methods fail to describe this modulus increase. As a consequence, we have developed a discrete numerical model starting from a two-phase assembly (e. g.³), which takes into account (i) the microstructure and (ii) the load transfer through the contact.

Calculations are made on a close packing of monodisperse spheres, which represent either the filler particles or the PBA matrix particles (≈ 1000 spheres with a packing density ≈ 0.57 , **Fig. 2**). At each contact between neighbouring spheres, three forces and three moments are transmitted. These efforts are expressed as a linear function of the displacements and the rotations of the connected spheres, exhibiting different “contact stiffnesses” (normal, tangential, flexural and torsional). These stiffnesses depend both on the modulus of each connected sphere and on a geometrical parameter α defined as $\alpha=(R_c/R)^2$, where R_c and R are the contact radius and the sphere radius respectively. In fact, the larger α (i. e. the contact area), the higher the transmission of moments through the contact.

Three kinds of contact are thus considered: soft/soft, hard/hard and soft/hard contacts. α^{ss} for soft/soft contacts is taken equal to 1, since the PBA matrix of nanocomposites materials is continuous. For hard/hard contacts, we used a variable α^{hh} in order to quantify the effect of the strength of filler-filler interactions on the effective modulus. Soft/hard contacts result from a serial law between hard/hard contacts (with $\alpha^{hh}=1$ since the PBA matrix totally wets filler particles) and soft/soft contacts ($\alpha^{ss}=1$). The effective modulus is then numerically deduced by applying adequate boundary conditions, corresponding to a compression test.

Fig. 3 shows the effect of the strength of hard/hard contact (i. e. α^{hh}) on the evolution of the packing modulus with the filler ratio. When filler-filler interactions are strong ($\alpha^{hh}=1$), the effective modulus increases suddenly at the geometrical percolation threshold $\phi_c=18.5\%$ vol. When filler-filler interactions are weaker ($\alpha^{hh}<10^{-2}$), i. e. when the rolling of hard particles is allowed, there is no discontinuity at the percolation threshold. The weaker the strength of filler-filler interactions, the lower the packing modulus. Experimental values obtained for PS-PBA nanocomposites at 60 °C in “as dried” and “annealed” states have been also reported on **Fig. 3**. After the annealing treatment, PS particles are strongly bonded. As a consequence, simulation calculations made with $\alpha^{hh}=1$ (efforts and moments are transmitted as in bulk PS) are in very good agreement with experimental data. Before the annealing treatment, the strength of filler-filler interaction is weaker and the value $\alpha^{hh}=1.35\times 10^{-2}$ allows one to account very well for all PS volume fractions.

LARGE STRAIN PROPERTIES: A MEAN FIELD APPROACH

The large strain behaviour of silica-P(S-BA) nanocomposites has been characterised by performing tensile tests around the glass transition temperature of the matrix ($-10<T<0^\circ\text{C}$).

To model the nonlinear behaviour of nanocomposites, the classical procedure of transforming, at a given strain, a nonlinear problem into a linear one has been used. This procedure is schematically presented in **Fig. 4**. The chosen linearisation method is the recently proposed affine formulation⁵ which has been coupled to a generalised self-consistent estimate⁶ of the linearised overall properties. The linearisation at the first order of the behaviour law $\sigma = f(\varepsilon)$ of each constitutive phase gives, at a given reference strain ε_0 :

$$\sigma = \sigma_0 + \left[\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon_0} : (\varepsilon - \varepsilon_0) = L^{igt}(\varepsilon_0) : \varepsilon + \tau(\varepsilon_0)$$

where $\tau(\varepsilon_0) = \sigma_0 - L^{igt}(\varepsilon_0) : \varepsilon_0$

defining thus, for each phase, a linear thermoelastic comparison medium based on tangent modulus. In case of an isotropic material loaded in uniaxial tension, this tangent modulus is transversally isotropic (5 constants). The effective properties L^{eff} of the obtained heterogeneous linear comparison medium made of the linearised behaviours of the matrix and of the filler phase are estimated using the generalised self-consistent model devoted to matrix-inclusion morphology. This linear step is resolved numerically by the finite elements method because of the anisotropic tangent behaviour. The reference strain ε_0 for each phase are chosen such that they are equal to the average strain in the corresponding linearised phase and are solution of the nonlinear set of equations solved iteratively. Having estimated L^{eff} , the macroscopic behaviour ($\langle \sigma \rangle$, $\langle \varepsilon \rangle$) of the composite is then obtained as usually: $\langle \varepsilon \rangle = f_m \langle \varepsilon \rangle_m + f_i \langle \varepsilon \rangle_i$ and $\langle \sigma \rangle = L^{eff} : \langle \varepsilon \rangle + \tau^{eff}$.

As an illustration, **Fig. 5** compares simulated and experimental data for 25% silica filled P(S-BA) nanocomposite. The good agreement between simulation and experimental data suggests that the filler network, whose influence is predominant in the linear domain, may have been broken as early as one percent of deformation.

CONCLUSION

In the linear domain, the main influence of the presence of the nanosized filler in an acrylate matrix is observed in the rubbery plateau. In this temperature range, the linear mechanical behaviour seems to be essentially governed by the microstructure and the strength of the links between the filler, these links being either direct contacts or indirect contacts via the matrix in-between. To account for the observed increase of modulus, a discrete model of spheres assembly taking into account the local filler/filler and matrix/filler contacts is proposed which agrees well with the experimental data and allows one to better understand the reinforcement when the percolation threshold is crossed. However, in the nonlinear domain, a mean field approach coupling the affine linearisation method and the generalised self-consistent estimate appears to be relevant for predicting the evolution of the stress beyond the yield point.

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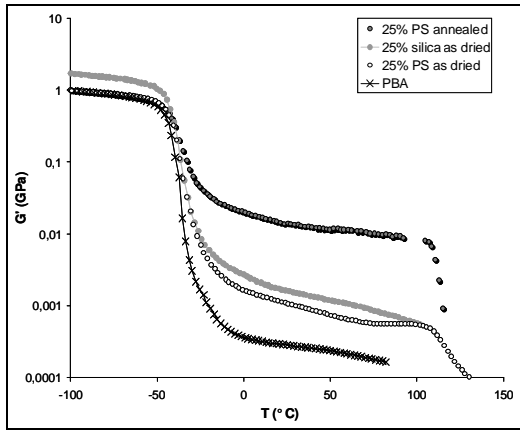


Fig. 1: Elastic shear modulus of “as dried” and “annealed” PS /PBA nanocomposites and silica/PBA nanocomposites as a function of temperature (1 Hz, 1°C/min).

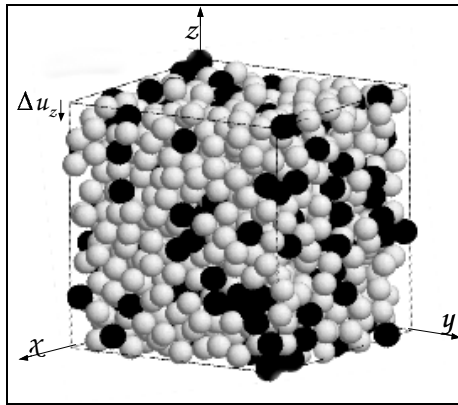


Fig. 2: Example of random packing of monodisperse hard and soft spheres used to calculate the effective elastic modulus.

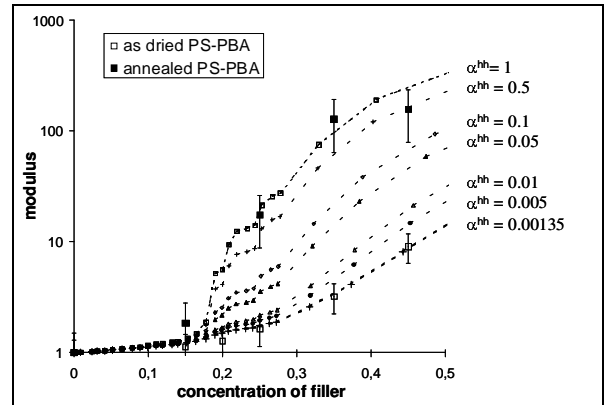


Fig. 3: Real shear modulus of PS-PBA nanocomposites at 60°C before and after the annealing treatment. Modelling with the discrete numerical simulation varying the strength of filler-filler interactions (α^{hh}).

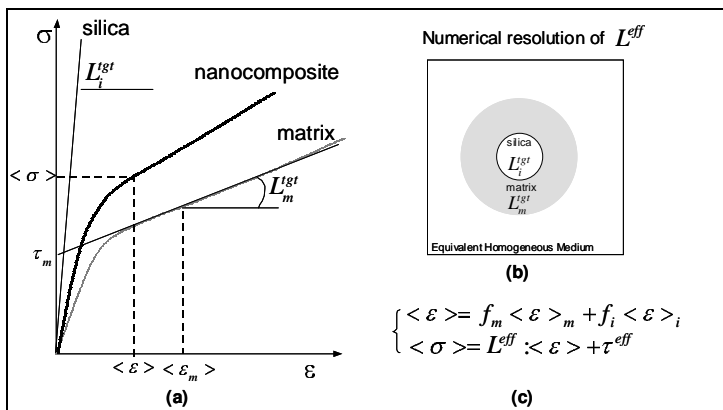


Fig. 4: Modelling of non linear stress-strain curve by homogenisation techniques (a) Linearisation using the affine method (b) resolution of the linear problem by the finite elements method (c) calculation of the nanocomposite stress-strain curve.

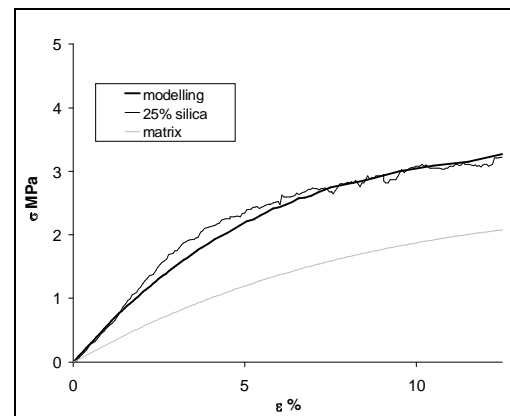


Fig. 5: Tensile curve of 25% silica-P(S-BA) nanocomposites (-5°C, $\dot{\epsilon} = 1.33 \times 10^{-2} \text{ s}^{-1}$). Modelling by homogenisation techniques.