Constraints effects in swollen particulate composites with hyperelastic polymer matrix of finite extensibility modeled by FEM

Ján Šouvarský¹, Karel Dušek² and Miroslava Dušková-Smrčková¹,²

¹ Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 180 00 Prague, Czech Republic
² Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský sq. 2, 162 00 Prague, Czech Republic
E-mail: jan.souvarsky@mff.cuni.cz, dusek@imc.cas.cz, miroslava.duskova@imc.cas.cz

Abstract. The class of particulate composites with cross-linked hyperelastic polymer matrix and non-deformable filler particles represents many important biopolymer and engineering materials. At application conditions, the matrix is either in the swollen state, or the swollen state is utilized for matrix characterization. In this contribution, a numerical model for simulation of equilibrium stress-strain and swelling behavior of this composite material was developed based on finite element method using COMSOL Multiphysics® software. In the constitutive equations (Gibbs energy), the elastic contribution is based on statistical-mechanical model of a network composed of freely jointed chains of finite extensibility and polymer-solvent mixing term is derived from the Flory-Huggins lattice model. A perfect adhesion of matrix-to-particle is assumed. The adhesion of matrix to stiff surface generates stress and degree-of-swelling fields in the composite. The existence of these fields determines the mechanical and swelling properties of the composite. Spatial distribution of filler particles in the composite plays an important role.

1. Introduction
Particle-filled composites with cross-linked polymer matrix and solid fillers are one of important classes of materials such as construction materials, high-performance engineering materials, sealants, protective organic coatings or dental materials. At application conditions, the matrix is either rubbery or glassy, but the glassy matrix can be transferred into the rubbery state either by increasing the temperature above the glass-transition temperature, $T_g$, or by decreasing $T_g$ by swelling. Swelling test can distinguish cases of good and poor adhesion between the filler and the matrix; if the adhesion is poor, the filler is debonded from the matrix by swelling stresses and voids filled with liquid are formed. This communication is concerned with the composites, in which the adhesion is good and it is not affected by swelling. Also, we will be concerned with the case of relatively large particles (in micrometer range) and not with nanocomposites, in which the change of polymer chain conformation close to the interface and decreased segment mobility make important contributions to mechanical properties [1]. However, for cross-linked matrix the constraints caused by bonding of polymer chains to the filler surface are transmitted by the network of polymer chains deeply into the bulk matrix phase at distances of an order of...
magnitude of filler particles radii. Many factors control the response to stresses imposed on the composite by external deformation or swelling, such as volume fraction of filler, size and shape of the filler particles, and spatial distribution of filler particles in the matrix.

2. Simulation procedure

2.1. Selection of the Gibbs energy

The Gibbs energy change for deformation of the network by swelling and other internal and external constraints was based on the three-chain model of Wang and Guth [2] expanded into a polynomial form by Smith et al. [3] in term of powers of $1/n$, where $n$ is the number of statistical segments in a network chain.

$$\frac{\Delta G_{\text{net}}}{RT} = N_e \left\{ \frac{1}{2} \left( 1 + \frac{4}{5n} \right) \left( \lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) + \frac{3}{10n} \left( \lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)^2 + \frac{2}{5n} \left( \lambda_x^2 \lambda_y^2 + \lambda_x^2 \lambda_z^2 + \lambda_y^2 \lambda_z^2 - 3 \right) \right\} - N_e \ln(\lambda_x \lambda_y \lambda_z)$$  (1)

The mixing of polymer with solvent is taken as a simple sum of the combinatorial entropy and the van Laar pairwise interaction term

$$\frac{\Delta G_{\text{mix}}}{RT} = N_1 \ln \phi_1 + g(\phi_2) N_1 \phi_2$$  (2)

The total Gibbs energy change then reeds

$$\Delta G_{\text{sw}} = \Delta G_{\text{net}} + \Delta G_{\text{mix}}$$  (3)

In these equations, $N_1$ and $N_e$ are numbers of moles of the solvent and elastically active network chains (EANC), respectively, and $n$ is the number of statistical segments per EANC, $T$ is temperature in Kelvin and $R$ is the gas constant; $\lambda_i$ are the deformation ratios relative to the reference state. Affine deformation model is considered. The isotropic state at network formation is considered to be the reference state. The quantity $g(\phi_2)$ is the concentration dependent interaction function [4, 5] which is related to the concentration dependent interaction parameter $\chi(\phi_2)$ introduced in the expression for the chemical potential of the solvent (after differentiation of $\Delta G_{\text{mix}}$ with respect to $N_1$): $\chi(\phi_2) = g(\phi_2) - (1 - \phi_2)g'(\phi_2)$

2.2. Representative volume element (RVE)

The model of composite is based on the choice of a representative volume element (RVE) which is periodically repeated in all three dimensions. We used simple RVE’s as a cube of polymer with one spherical filler particle in its center – simple cubic lattice (SC), body centered cubic lattice (BC) and face centered cubic lattice (FCC), and RVE’s composed of $N \times N \times N$ smaller cubes, some of them being occupied by spheres, $N = 2 – 6$. The $N \times N \times N$ RVE’s are suitable for study of the effect of space distribution of filler particles.

An important parameter is the minimal distance between filler particles (the distance between nearest neighbours). At the given volume fraction of filler particles, the minimal distance decreases in the sequence of models FCC, BCC, SC, $N \times N \times N$.

2.3. Periodic conditions

The periodic conditions are aimed to ensure the same deformation of the counterpart boundaries allowing changes of their size and shape (planar boundaries can be deformed even to non-planar ones) and mutual distance, which is satisfied by:

$$\mathbf{u}(0, Y, Z) - \mathbf{u}(0, 0, 0) = \mathbf{u}(a_0, Y, Z) - \mathbf{u}(a_0, 0, 0)$$
for $x$ direction, and similarly for $y$ and $z$ directions, where $\mathbf{u} \equiv (u, v, w)$ is the displacement vector and $a_0$ is edge length of RVE. Using the COMSOL Multiphysics® package, such periodic conditions can be implemented via functions “Similarity boundaries” and “Prescribed displacement”. Note that the function “Periodic conditions” does not allow changing of distance between the counterpart boundaries due to deformation (like $\mathbf{u}(0,0,0) - \mathbf{u}(a_0,0,0)$ resulting from swelling and shear or tension).

2.4. Meshing suitable for periodic repetition using COMSOL Multiphysics®
The counterpart boundaries in periodic repetition should have the same mesh. Simply meshing a boundary faces and copying these meshes to the counterpart faces (in all three dimensions) is not usable: it ignores possible effect of objects close to the face. In order to generate a correct mesh, it is necessary to mesh 3D domains around boundary edges and faces. In the space filled with periodically repeated RVE’s, we select cubes of the size of RVE around boundary edges and faces in all three dimensions, and obtain $3 + 3 = 6$ auxiliary objects (Fig. 1). A correct mesh generating procedure consists in meshing edge objects, copying the edge meshes to face objects, meshing face objects and copying the face meshes to RVE, and finally meshing the RVE (with given boundary face meshes). The COMSOL Multiphysics® is able to work with auxiliary geometry objects and solve the problem just for selected objects, in our case for the RVE.

3. Results and discussion
The stress field and profiles of the degree of swelling generated in a simple element – matrix coated rigid sphere with good adhesion of matrix to the filler – is shown in Fig. 2. The adhesion generates in equilibrium with the outer pure liquid a gradient profile in the amount of imbibed liquid by the matrix. The degree of swelling increases onwards asymptotically reaching the value for the degree of swelling of unconstrained matrix. Unconstrained swelling is characteristic for matrix if debonding occurs due to a poor adhesion – a situation shown in the lower part of Fig. 2 where debonding of the matrix from the filler occurred.

The stress and swelling degrees fields are different in the composite because the compressed parts of the matrix tend to expand and to generate expansive stresses causing parts of the network to swell more than the unconstrained, free matrix. The situation is illustrated by
Fig. 3 where the expanded regions coincide with regions of the highest stress. These regions are identical with the regions of the closest distance between neighboring particle surfaces.

The constraints by the filler and the resulting spatial distribution of swollen matrix composition and properties have a number of effects on the physical and engineering properties of the composites. The degree of swelling of the matrix generally decreases, the equilibrium shear and tensile moduli increase. At the same time, the spatial distribution of filler particles plays an important role. The effect of volume fraction of filler for composites with regularly distributed particles is weak at low degrees of filling because all particles are far apart from each other; however, at high degree of filling the interparticle distances for all particles get small simultaneously which results in a steep decrease of the degree of swelling and increase of the modulus of elasticity. For irregularly (e.g., randomly) distributed filler, the particles approach their neighbors gradually and the change of properties is flatter (Fig. 4).

The results of simulation performed for swelling of composites of cross-linked poly(methyl methacrylate) matrix filled with nearly spherical alumina filler of 10 µm size were in a relatively good agreement with experiment.

4. Conclusions
The simulation of thermodynamic and transport properties of swollen composites is important especially for the design of filled hydrophilic gels where the swelling degree can be very high and the reinforcing effect very useful. The study of filled highly-swollen hydrogels is our future task; we also want to concentrate on the swelling dynamics using the theory of diffusion in soft matter. The advantage of the COMSOL Multiphysics® is the support of user defined parameters and equations, including elastic potential $\Delta G_{sw}$ and the interaction with MATLAB – the model can be written in MATLAB programming language using COMSOL functions.

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