

Meso-scale Dynamic of Polymeric Glasses: Constitutive Models that Acknowledge Dynamic Heterogeneity

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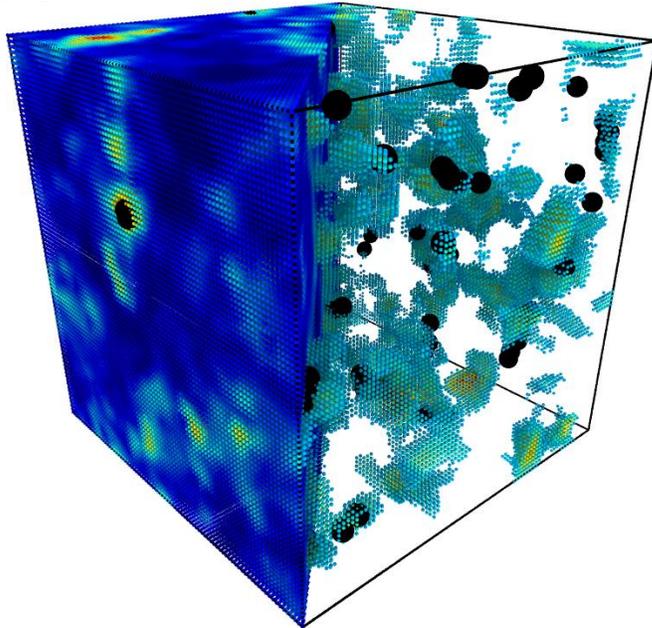
The current physical picture of the glassy state involves dynamic heterogeneity, where nanoscopic regions of the glass have order-of-magnitude differences in local mobility even though the structure appears to be uniform. Moreover, these nanoscopic regions evolve with time where high mobility regions can become low mobility regions and vice-versa. Dynamic heterogeneity provides a critical challenge to the traditional nonlinear viscoelastic or viscoplastic continuum models where both temporal and spatial fluctuations are smoothed out as a result of the continuum postulate. In order to acknowledge dynamic heterogeneity, a Stochastic Constitutive Model (SCM) has been developed to describe the nonlinear viscoelastic behavior of polymeric glasses, where temporal fluctuations are explicitly included but spatially fluctuations are averaged in a mean field like approximation. In addition to the fluctuations, a key feature of the SCM is that the local mobility depends upon the local state of the material (e.g. local stress and local entropy) vs. the nonlinear viscoelastic/viscoplastic models where macroscopic mobility depends upon the macroscopic state. The SCM is able to describe a number of nonlinear relaxation phenomena that cannot be predicted by traditional nonlinear viscoelastic/viscoplastic models, including (i) post-yield stress softening and its dependence on annealing time, (ii) the inversion of the strain dependence of nonlinear stress relaxation with the loading rate and (iii) tertiary creep and creep-recovery. Because the SCM includes fluctuations, the SCM may provide an effective mesoscopic link between molecular dynamic simulations where fluctuations are significant and continuum models that can predict the response for engineering useful times.

Predicting segmental relaxation in quiescent and deformed polymer glasses

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Structural recovery and plastic flow in polymer glasses occurs in a highly heterogeneous fashion through cooperative segmental relaxation events. While simulations have elucidated many aspects of this dynamical heterogeneity, the connection to structural properties has remained elusive. In this contribution, we show that the low energy



Softness map of a polymer glass with softness increasing from blue to red. Cutaway shows only the top 10% softest regions. Black dots indicate the location of structural relaxation events in a small time interval right after the map was constructed.

vibrational spectrum of the amorphous polymer can be used to predict the location and direction of segmental motion. A “softness field” is constructed from a superposition of the amplitudes of the lowest energy normal modes, which reveals essentially the elastic heterogeneity of the solid.

Segmental relaxation events are identified as discrete “hops” of particles out of their local cages with a numerical technique developed previously [1]. We find that these hops occur preferentially at the softest regions in the polymer. Moreover, the *direction* of the hops can be accurately predicted from the direction of the normal mode polarization field (a harmonic property). Thus, the soft modes predict not only where the

polymer will relax, but also how. We explore the evolution of the correlation between softness field and relaxation events for different temperatures, different ages, and for active deformation with molecular dynamics simulations of a coarse-grained bead-spring polymer model. The softness field decays very slowly (logarithmically) on time scales much longer than the vibrational timescale, which indicates that it is a robust structural feature suitable to detect local regions vulnerable to irreversible relaxation events. Parallel work on models for amorphous metals suggests that these “soft spots” are indeed the counterpart of dislocations in disordered materials.

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Filled polymer glasses; the sum of its parts?

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Since polymers play an increasingly important role in both structural and tribological applications, understanding their intrinsic mechanical response is key [1]. Therefore, much effort has gone into the development of models, such as the Eindhoven Glassy Polymer (EGP) model [2], which captures the polymers' response quantitatively. In practice, however, these polymers are filled, e.g. with colorants and impact modifiers.

To characterize the effect of filler particles on the intrinsic mechanical response, model systems of polycarbonate and epoxy are filled with either hard (TiO_2) or soft (MBS) particles and tested in uniaxial compression. Since experimentally only macroscopic effects are probed, simulations are needed to reveal the effects at the inter-particle level. Therefore, representative volume elements (RVEs) are constructed, where the matrix material is modeled with the EGP model and the fillers with their individual mechanical properties.

Comparing the simulated response of the RVEs with the experiments shows that the macroscopic response is captured well. Only at large deformations the simulations fail to capture the response of the hard-filled system. Moreover, the simulations clearly show that all the rate-dependence originates from the polymer matrix; fillers only change the magnitude of stress.

In the simulations it is assumed that the particles perfectly adhere to the matrix. In reality, for the hard-filled system, this interface or the polymer itself will fail at some point; the local strains significantly exceed the macroscopic applied deformation. But since the local deformations are now available quantifying the onset of failure is within reach. Subsequently, this method proves to be beneficial as a design tool too: different scenarios, e.g. altering or even combining filler properties, are easily tested without the need of tedious experiments.

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[2] Van Breemen et al., *J. Mech. Phys. Solids* 2011, 59(10), 2191-2207

Hierarchical composites reinforced with microscopic fibers and nanotubes: the modelling challenge.

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The toughness improvement of fiber reinforced polymer composites is an important area of research in the field of composites. Despite superior strength and stiffness, these materials are susceptible to early onset of matrix cracking. The cracks start as debonding at the fiber/matrix interface where high stress concentrations are generated and then develop through the matrix into larger cracks. This type of damage can be suppressed by adding carbon nanotubes (CNTs) into the polymer matrix of the composite or by growing CNTs directly on the fiber surface [1]. There are several possible explanations for the toughening effect. One of them is a re-distribution of stresses on the micro-scale caused by the presence of CNTs.

In order to investigate a hypothesis that CNTs can have a significant effect on stress concentrations, we developed an advanced two-scale model. The unique feature of this model is that microscopic fibers and nanotubes are modelled simultaneously. The challenge lies in modeling of reinforcements with a significant difference in relative dimensions— diameters carbon fibers and CNTs differ more than 700 times. Recent literature survey showed that there are no models of nano-engineered composites that are able to meet such a requirement.

In the present work we introduce the 3D FE model, in which CNTs are represented as 3D solid bodies implemented into a polymer already reinforced with microscopic carbon fibers. It was achieved with the embedded regions (ER) technique that allows for co-existence of two independent FE meshes. The model does not require intermediate homogenization steps or transferring of parameters from the nanotube scale to the fiber scale. The effect of different CNT configurations on stress fields in the matrix is investigated.

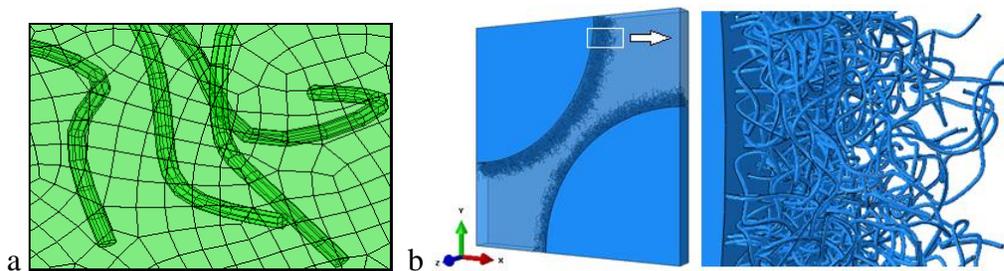


Figure 1: (a) ER technique - the combination of two independently created FE meshes: CNT mesh and matrix mesh; (b) a 3D model of a unidirectional fiber reinforced composite with introduced CNTs showing the unit cell and the zoom-in on the geometry of the grown CNT forests on the fiber surfaces.

This model was developed in the IMS&CPS project (Innovative Material Synergies & Composite Processing Strategies) funded by the EU FP7 program. The analysis of CNT configurations was performed in the framework of the GOA/10/004 project (New model-based concepts for nano-engineered polymer composites) funded by the Research Council of KU Leuven.

[1] De Greef, N., et al., Carbon. **49**,14 (2011).

Concurrent two-scale model for the elasto-viscoplastic behavior of silica-filled rubber

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A dynamic two-scale model for describing the mechanical behavior of silica-filled elastomers is developed. The closed system of evolution equations is derived, consisting of evolution equations for the macroscopic momentum density, the temperature, the macroscopic deformation gradient and a mesoscale structure variable. The latter is given by the product of the number density of filler particles and the distribution function of particle-particle separation vectors. The system under consideration is strongly non-linear. The origins of non-linearity are the following: (i) the rubbery matrix, in which the particles are imbedded, expresses non-linear elastic effects; (ii) around the nanofillers, the matrix material forms glassy layers that overlap for sufficiently close particles, and consequently create temporary glassy bridges with a characteristic time scale that depends on the applied load (e.g. [1]). Extending earlier efforts to model nonisothermal and finite-deformation elasto-viscoplasticity [2, 3] with the GENERIC framework of nonequilibrium thermodynamics [4, 5, 6], we obtain the constitutive relation for the macroscopic stress tensor in terms of the filler-particle arrangement. Moreover, the filler-particle dynamics and the thermodynamic driving force for the breaking and recombination of the glassy bridges are derived. Finally, it is shown that the mesoscale dynamics can be cast into a stochastic differential equation in 6-dimensional space, amendable to Brownian dynamics-type simulations on the filler-particle level.

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- [3] M. Hütter, T.A. Tervoort, *J. Non-Newtonian Fluid Mech.* **152**, 53 (2008).
- [4] M. Grmela, H.C. Öttinger, *Phys. Rev. E* **56**, 6620 (1997).
- [5] H.C. Öttinger, M. Grmela, *Phys. Rev. E* **56**, 6633 (1997).
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Micromechanics modeling of the linear viscoelasticity of nano-reinforced polymers with an interphase

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A first study [1] showed experimental evidences and micromechanics analysis supporting the existence in carbon-black filled styrene butadiene rubbers, of a filler-rubber interphase with viscoelastic properties and reduced mobility due to the possible confinement at the particle-matrix interface.

Using a simple spherical rigid representation for the carbon-black and a viscoelastic behavior for the rubber within the 4-phase model [2], it has been possible to determine the viscoelastic behavior of the interphase and its thickness was estimated to 5 nm.

In order to discuss this arguably reasonable value of 5 nm, the self-consistent model based on morphological representative pattern [3] was applied. Such a model introduces microstructure parameters such as the particle dispersion, particle size distribution or interparticle distance distribution allowing the study of the impact of such parameters on the material viscoelasticity. Results show that the 4-phase model give an upper bound of the interphase thickness and that the particle dispersion and the interparticle distance distribution have a significant impact on the nanoparticle reinforced polymer while the particle distribution has little effect [4].

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Coupled Digital Image Correlation and Fracture Mechanics analysis for the identification of cohesive models in polymers at the micron scale

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We present a new methodology [1] for the identification of a cohesive model which describes the material's failure. The goal is twofold: (i) to provide insight in the mechanism underlying failure and (ii) derive information for a realistic description within a cohesive model approach. The material under consideration is a thermoplastic (PMMA) which is known to fail by crazing. PMMA has been elected as the size of its process zone is of few microns in opening with a process zone tens of microns long. A sample of PMMA with a natural crack is tested under four points bending. The study is conducted at the micron scale with the observation of the displacement fields at the notch tip. These are measured optically by Digital Image Correlation. In a first analysis, the displacement is searched for as a decomposition over Williams' series [2]. As shown in [3], it allows for extracting not only stress intensity factors but also the position of the crack tip. The equivalent elastic crack is thus determined as the crack within a perfectly elastic material which produces the same far-fields. The evolution of the equivalent elastic crack position is obtained from this analysis. The advance of this tip during the test corresponds to the development of crazing within a cohesive zone. In a second step, X-FEM simulations with a cohesive model are performed using the displacement obtained by DIC as boundary conditions. The obtained displacement field is projected onto the Williams' series so that the equivalent elastic crack from the X-FEM simulation is determined. The parameters of the cohesive law are then adjusted so that the gap between the crack tip position obtained the experimental analysis and the numerical simulation is minimized. For the PMMA under consideration, the methodology allows to capture the onset of crazing, the traction- separation profile and the maximum opening corresponding to the nucleation of a crack locally. The identified cohesive parameters are consistent with results available in the literature. In addition, the model enables the characterization of the normal and tangential mode of the cohesive model. Further, the proposed methodology allows to access to the mechanical state inside the cohesive law whereas its length is far smaller than the usual resolution of DIC. The methodology is exemplified in a fracture test on PMMA but the framework allows for investigation of the cohesive zone between in other polymers in which no cohesive zone are available at the moment and cohesive zone representing the interface between assembled bulk part.

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A Thermodynamically Consistent Finite Deformation Enhanced Strain Formulation for the Coupled Diffusion in Gels

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This presentation is concerned with the development of a large-deformation, continuum-level theory to describe the coupling of the interaction of mechanics and chemistry for polymeric networks, capable of absorbing fluid-like chemical species. The mixture of solid and solvent is treated as a homogenized continuum. To avoid numerical difficulties, a new approach for the approximation of the different field variables is presented in the context of the finite element method. In particular, an enhanced strain formulation within the finite deformation context is proposed to avoid otherwise resulting diffusion driven locking phenomena. A thermodynamically-consistent theory that is in full agreement with the supposedly incompressible behavior of both the solid and the solvent phase of the mixture is presented. The change in entropy due to mixing the fluid and the polymer network is based on the Flory-Huggins model and the change in the configurational entropy due to stretching the network is based on a model for Gaussian chains. A statistical mechanics approach for a pre-swollen reference configuration is presented. Several numerical simulation outline the performance of the new approach.

Micromechanical modeling of elastoplastic damage behavior of the human femur under compression loading

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Osteoporotic hip fractures represent a burden of mortality on the growing population of old patients. To estimate hip fracture and plan the preventive intervention, the strength of the proximal femur must be precisely quantified. To this end, computed tomography based Finite Element analysis which incorporates information on both 3D architecture and bone density, can be used. Furthermore, micromechanical approaches coupled with CT-based FE models were revealed to be more appropriate when the robustness of computation and accuracy of results are of interest.

In this study we propose a micromechanical elastoplastic model of the human femur bone behavior in view of an integration of bone damage for the simulation of necking and rupture initiation. The damage is carried out by the framework of the limit analysis based on the MCK criterion [1]. We first present the methodology allowing the estimation of elastic anisotropic properties of porous media by means of the Mori-Tanaka homogenization scheme [2]. Then, we develop the formulation of the integrated yield criterion derived by considering trial velocity field inspired from the Eshelby inhomogeneous inclusion solution [3]. The obtained micromechanical model is implemented via a User Material routine within the explicit dynamic code LS-DYNA. To illustrate the potential of the current approach, a right adult human femur was simulated until complete fracture under sideways loading.

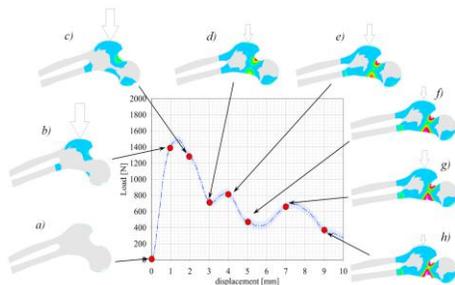


Figure 1: Damage evolution in the cancellous femoral bone during compression loading.

The obtained numerical load-displacement response matches globally the experimental results. Our results showed progressive fracture profiles depending on the vertical trochanter stroke (see Figure 1). The predicted fracture path follows a diagonal line from the inner surface of the neck (basal) to the outer surface towards the greater trochanter. A comparison between predicted fracture path and radiographs of basicervical fractures from the literature shows a quite good agreement, even if loading conditions may be different. Thus, the proposed micromechanical model improved the strength prediction of metastatic femurs by representing the failure risk in a more realistic approach.

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