Investigation of the Mechanical Behavior of Polystyrene using Molecular Dynamics

Maximilian Ries1,∗, Paul Steinmann1,∗∗, and Sebastian Pfaller1,∗∗∗

1 University of Erlangen-Nuremberg, Chair of Applied Mechanics, Egerlandstr. 5, 91058 Erlangen

Polymer nanocomposites exhibit highly promising material properties caused by their molecular structure. Multiscale techniques are used to gain a deeper understanding of the influence of molecular mechanisms on the macro scale. Especially domain composition coupling approaches, e.g. the Capriccio method [1], require a precise match of the constitutive models of the coupled domains. To this end, in this contribution a methodology to characterize the material behavior of polymers using the widely used Molecular Dynamics approach is presented. Exemplary, polystyrene is investigated as a model system and the results of time proportional and time periodic uniaxial deformation tests as well as relaxation and creep tests are briefly discussed.

© 2019 The Authors Proceedings in Applied Mathematics & Mechanics published by Wiley-VCH Verlag GmbH & Co. KGaA Weinheim

1 Introduction

Polymer nanocomposites are becoming increasingly important as design material in modern engineering solutions. Their desired properties follow from mechanisms at the molecular level which are not well understood yet. Due to the very small time and lengths scales, experimental investigations become either prohibitively expensive or simply impossible. Classical simulation techniques are not an option, too, since continuum approaches cannot cover molecular mechanisms while particle-based methods cannot reach engineering time and lengths scales. One possible solution is the combination of these classical approaches in so called multiscale techniques. These methods, however, require a precise material model of the constitutives of the nanocomposite in order to obtain reasonable and reliable results. The Capriccio method introduced in [1] couples a particle domain with a continuum and is used i.a. to investigate the effects of nano-sized silica additives embedded in atactic polystyrene (PS) [2]. The particles are modeled with Molecular Dynamics (MD) and so far, a simple hyperelastic constitutive law is used for the continuum description. To further enhance the quality of the results, the material model should be derived directly from MD simulations under thermodynamic conditions identical to those used by the Capriccio method. The first step in this endeavor is the characterization of the material response of pure polystyrene (PS) under uniaxial deformation using strain-controlled MD simulations.

2 Uniaxial tension within Molecular Dynamics

In MD the interactions between all particles, given e.g. as force fields, are evaluated to determine the trajectories of the particles by solving NEWTON’S equations of motion. Ensembles are used to isolate the system from changes of certain thermodynamic quantities. In our case, the number of particles and the temperature are kept constant. Furthermore, we want to prescribe the deformation in one direction while allowing a free contraction in the other two directions. This is achieved by applying the canonical (NVT) ensemble in tensile and the isothermal-isobaric ensemble (NPT) in lateral directions.

Using this set up, we apply a time proportional load of $\lambda_2 = 1.08$ in tensile directions and time periodic loads with amplitudes of $\lambda_x = 1.01 \ldots 1.08$ both with stretch rates from $0.1 \%\text{s}^{-1}$ to $20 \%\text{s}^{-1}$.

Our model system consists of 300 PS chains with 200 monomers each, generated with a random-walk algorithm implemented by [4]. This results in cuboid systems with an edge length of approximately $21 \text{nm}$ and 180,000 DOFs at coarse-grained resolution [6]. To obtain statistically reliable results, 10 slightly different of these systems are investigated using the MD solver IBiSCO [5].

Time periodic simulations performed independently in $x$-, $y$– and $z$– direction reveal isotropic behavior of the present polystyrene. Thus, all further investigations are conducted in $x$– direction.

Under time proportional loading, the material responds stiffer with increasing deformation rate, c.f. Fig. 1, indicating a rate dependence which is characteristic for viscous materials.

The equilibrium stress-strain hystereses obtained in time periodic simulations indicate the presence of inelastic effects. However, an elastic range up to $2 \%$ strain is identified where almost no energy is dissipated. For larger strains, the dissipated energy density and thus the inelasticity increase quadratically. Whether this can be explained solely by viscous effects or if visco-plasticity has to be taken into account, is examined in relaxation tests.

Corresponding author: maximilian.ries@fau.de,

** paul.steinmann@fau.de

*** sebastian.pfaller@fau.de

This is an open access article under the terms of the Creative Commons Attribution License 4.0, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Received: 12 March 2019 Accepted: 5 April 2019 DOI: 10.1002/pamm.201900015

© 2019 The Authors Proceedings in Applied Mathematics & Mechanics published by Wiley-VCH Verlag GmbH & Co. KGaA Weinheim
3 Relaxation tests

The basic idea is to choose the starting points for these tests in such a way that elastic effects are already eliminated. At the end of the first stress-strain hysteresis, denoted by point $P_r$, zero strain is reached and thus the elastic part of the stress has to vanish. In a subsequent simulation, the deformation is kept constant, i.e. $E_{xx} = 0$, and the response of the remaining inelastic part of the stress is observed, c.f. Fig. 2. The viscous stress degrades over time due to relaxation processes which are more pronounced for larger preceding strain amplitudes. As a consequence, the remaining stress has to be caused by plasticity. Similar results are obtained from analogously performed creep tests.

Fig. 1 Influence of strain rate: Cauchy stress in tensile direction $\sigma_{xx}$ over Green-Lagrange strain in tensile direction $E_{xx}$ for time proportional uniaxial tension tests with maximum strain $E_{xx} = 8.36\%$ and initial strain rates from $E_{xx} = 0.1\%s^{-1}$ to $20\%s^{-1}$, distribution within measurement groups visualized by box plots.

![Graph showing Cauchy stress vs. Green-Lagrange strain](image)

Fig. 2 Identification of plasticity on the basis of relaxation tests with $E_{xx} = 0\% = \text{const}$ and with preceding cyclic loading with different strain amplitudes $E_{xx}^0$, extrapolation of simulation data with rational functions.

![Graph showing Cauchy stress vs. relaxation time](image)

4 Summary and outlook

As a conclusion, the present PS is isotropic and exhibits visco-plastic material behavior with a small elastic range. The applied methodology, however, can be used to investigate and characterize other polymers, too.

In order to obtain a more comprehensive understanding, we have to consider shear deformations as well. The gained insights will then provide the basis for the selection of a suitable material model whose parameters will be found in a subsequent parameter optimization.

References

[1] S. Pfaller, M. Rahimi, G. Possart, P. Steinmann, F. Müller-Plathe, and M. Böhm, COMPUT METHOD APPL M 260, 109-129 (2013).
[2] S. Pfaller, G. Possart, P. Steinmann, M. Rahimi, F. Müller-Plathe, and M. Böhm, PHYS REV E, 93, 052505 (2016).
[3] M. Ries, P. Steinmann, and S. Pfaller, Manuscript in Preparation (2019).
[4] A. Ghanbari, T. V. Ndroo, F. Leroy, M. Rahimi, M. C. Böhm and F. Müller-Plathe, Macromolecules 45 (1), 572-584 (2011).
[5] H. A. Karimi-Varzaneh, H.-J. Qian, X. Chen, P. Carbone and F. Müller-Plathe, J. Comput. Chem. 32 (7), 1475-1487 (2011).
[6] H.-J. Qian, P. Carbone, X. Chen, H. A. Karimi-Varzaneh, C. C. Liew, and F. Müller-Plathe, Macromolecules 41 (24), 9919-9929 (2008).