Journal of the Mechanics and Physics of Solids 87 (2016) 51–64

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Global and local large-deformation response of sub-micron, soft- and hard-particle filled polycarbonate

Sam Krop, Han E.H. Meijer, Lambert C.A. van Breemen *

Polymer Technology, Department of Mechanical Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form
16 November 2015
Accepted 21 November 2015
Available online 22 November 2015

Keywords:
A. Microstructures
B. Particulate reinforced material
B. Constitutive behaviour
C. Finite elements
Representative volume element

ABSTRACT

Since polymers play an increasingly important role in both structural and tribological applications, understanding their intrinsic mechanical response is key. Therefore in the last few decades much effort has been devoted into the development of constitutive models that capture the polymers' intrinsic mechanical response quantitatively. An example is the Eindhoven Glassy Polymer model. In practice most polymers are filled, e.g. with hard particles or fibers, with colorants, or with soft particles that serve as impact modifiers. To characterize the influence of type and amount of filler particles on the intrinsic mechanical response, we designed model systems of polycarbonate with different volume fractions of small, order 100 nm sized, either hard or soft particles, and tested them in lubricated uniaxial compression experiments. To reveal the local effects on interparticle level, three-dimensional representative volume elements (RVEs) were constructed. The matrix material is modeled with the EGP model and the fillers with their individual mechanical properties. It is first shown that (only) 32 particles are sufficient to capture the statistical variations in these systems. Comparing the simulated response of the RVEs with the experiments demonstrates that in the small strain regime the stress is under-predicted since the polymer matrix is modeled by using only one single relaxation time. The yield- and the large strain response is captured well for the soft-particle filled systems while, for the hard-particles at increased filler loadings, the predictions are less accurate. This is likely caused by polymer–filler interactions that result in accelerated physical aging of the polymer matrix close to the surfaces. Modifying the S_a-parameter, that captures the thermodynamic state of the polymer matrix, allows us to correctly predict the macroscopic response after yield. The simulations reveal that all rate-dependencies of the different filled systems originate from that of the polymer matrix. Finally, an onset is presented to predict local and global failure based on critical events on the microlevel, that are likely to cause the over-prediction in the large-strain response of the hard-particle filled systems.

1. Introduction

Predicting the intrinsic mechanical response of polymers is one of the major challenges of material scientists. Constitutive models that quantitatively capture this intrinsic response are an essential part of the engineering tools and used in finite element methods (FEM) to help designing their structural applications. In practice most engineering polymer

* Corresponding author.
E-mail address: l.c.a.v.breemen@tue.nl (L.C.A. van Breemen).

http://dx.doi.org/10.1016/j.jmps.2015.11.005
0022-5096/

materials are composites since mixing combinations of existing polymers and reinforcements is usually a more cost-efficient route than developing new polymers based on new chemistry (Meijer and Govaert, 2003; Winey and Vaia, 2007). In composites the macroscopic response originates from the individual intrinsic responses of the constituents, their volume fractions, the spatial distribution, and the interfacial interactions (Pukánszky, 2005). Historically, in the absence of numerical techniques, this issue was addressed using approximations based on mean-field homogenization schemes (Eshelby, 1957; Hill, 1965; Mori and Tanaka, 1973; Christensen and Lo, 1979; Ju and Chen, 1994a,b; Torquato, 1998). With the introduction of computers more complex methods could be implemented, but originally still for simplified situations, such as restrictions to two-phase systems, simple elasto-plastic materials, moderate macroscopic strains, low filler fractions, and periodic distributions. Usually analyses were restricted to two-dimensional problems only, due to large computational costs (Gusev, 1997; Ohno et al., 2000; van Melick et al., 2003; Kari et al., 2007; Gunel and Basaran, 2013).

One of the first attempts to overcome these restrictions was by the group of Llorca (Segurado et al., 2002, 2003; Segurado and LLorca, 2002, 2006), who used unit cells containing several dozens of particles. They showed with FEM simulations that the mechanical response over different particle realizations presented little scatter provided that indeed a sufficient number of particles was present. Still, these systems consisted of simple elastic and elasto-plastic systems. With Pierard et al. (2007) a first attempt was made to model an elasto-viscoplastic (Perzyna model) system. The moduli of the two constituents differed less than an order of magnitude, and only the small strain regime was considered. Numerical results were only compared to other homogenization techniques only, not to actual experimental results.

Of particular interest in recent years is the class of so-called nanocomposites where high surface-to-volume ratio's make interfacial effects become more important. Often a third phase surrounding the nano-particles is introduced, the interphase, using one- or two-step modeling strategies. With the former strategy interphases are directly incorporated in the representative volume element (RVE), with the latter an 'effective particle' is introduced, homogenizing particle and interphase (Sheng et al., 2004; Li et al., 2011; Cricrì et al., 2012; Pahlavanpour et al., 2014). Also in these examples only the small-strain elastic regime was considered.

In this paper we will try to improve on these points by capturing the actual mechanical response starting with the intrinsic mechanical behavior of the polymer matrix. Upon homogeneous deformation, glassy polymers initially show a viscoelastic region which becomes progressively nonlinear with increased loading. At the yield point (the first maximum in the curve) the stress is sufficiently high to overcome intermolecular forces at the rate of deformation prescribed, allowing large-scale segmental motion of the polymer chains. The post-yield response displays two characteristic phenomena: (i) strain softening, the initial decrease of true stress with increasing true strain, which is related to a structural evolution that reduces the material's resistance to plastic deformation, and (ii) strain hardening, the increase in stress at high strains, which originates from the network of entangled polymer chains that orients with deformation. The macroscopic response of polymers is strongly determined by the interplay between these two effects: strain softening tends to destabilize the deformation leading to the formation of localized plastic deformation zones, while the evolution of these plastic zones strongly depends on the stabilizing effect of strain hardening. These concepts are employed in several 3-D constitutive models, such as the Boyce–Parks–Argon (BPA) model (Boyce et al., 1988; Arruda and Boyce, 1993), the Oxford Glass–Rubber (OGR) model (Buckley and Jones, 1995; Buckley et al., 2004; De Focatiis et al., 2010) and the Eindhoven Glassy Polymer (EGP) model (Tervoort et al., 1997; Klompen et al., 2005; Senden et al., 2012; van Breemen et al., 2011, 2012a).

The highly non-linear time-dependent behavior of polymers causes in filled polymer systems the macroscopic response to be dominated by a sequential yielding process throughout the total microstructure. Mean-field homogenization schemes are therefore useless beyond the small-strain regime. For the response at increased deformation, analyses are needed that incorporate the microstructure of the system in an RVE. The advantage of such an approach is that events at the interparticle scale are probed as well, as nicely demonstrated by van Melick et al. (2003) and Meijer and Govaert (2003) for two-dimensional RVEs of polystyrene and polycarbonate matrices filled with circular voids, where the matrix was modeled using the EGP-model. They showed qualitatively the effect of voids on the macroscopic response, and demonstrated that a hydrostatic-stress based craze-nucleation criterion could be used to predict brittle-to-ductile transitions.

Here again polycarbonate (PC) is used as model material for the matrix and hard- and soft-particle filled systems are prepared and tested in uniaxial compression. These model systems are captured by 3D RVEs in a finite element mesh. First the critical size of the unit cell or RVE is determined, i.e. the minimum number of particles in the system that is required to ensure its representative character. Subsequently, the optimal element size inside the RVE is investigated. Next compression tests are performed, and experimental results are compared with the macroscopic response as it follows from the numerical simulations. Finally the local response on interparticle level is investigated and discussed, using a critical hydrostatic-stress based criterion to predict local and finally global failure. This criterion proved successful in predicting craze nucleation in a vast range of glassy polymers such as polycarbonate, polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide), polysulphone, and (unplasticized) polyvinyl chloride (Ishikawa et al., 1977; Ishikawa and Narisawa, 1983; Kambour and Farraye, 1984; Nimmer and Woods, 1992; van Melick et al., 2003; Engels et al., 2011; Visser et al., 2011). The part of the work presented in this paper prepares for the modeling of soft- and hard-particle filled thermoset epoxies that finally will be modeled and tested as coatings in sliding friction experiments, analogous to van Breemen et al. (2012b).