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A three-scale framework for fibre-reinforced-polymer curing Part I: Microscopic modeling and mesoscopic effective properties

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ABSTRACT

Our work presents a three-scale model for temperature-dependent visco-elastic effects accompanied by curing, which are important phenomena in a resin transfer molding (RTM) process. In Part I, bounds for the bulk quantities of the matrix material in dependence of the degree of cure for an equally distributed, homogeneous mixture with phases resin, curing agent and solid are derived. Furthermore, effective bulk quantities are obtained by homogenization for a representative unit cell (micro-RVE) on the heterogeneous microscale, taking into account the geometrical arrangement of phases. To this end, an analytic solution is derived by extension of the *composite spheres model* known from the literature. For simplification, we restrict the material behavior of the micro-RVE to linear thermo-chemo-elasticity. In a study we compare different meso material properties including bounds and effective material constants. In the examples we compare the meso-micro relations for the homogeneous matrix with those derived for the heterogeneous matrix.

1. Introduction

Nowadays, polymeric materials play an important role in industry, where adhesives in automotive, electronics or aerospace industry are typical examples. Moreover, applications are found in carbon- and glass fibre-reinforced composite materials, epoxy laminates and (nano-)particle-reinforced polymer structures, e.g. in the works of Ruiz and Trochu (2005) or Lange (1999). The matrix in the initial uncured state, a mixture of resin and curing agent, exhibits a viscous liquid behavior until gelation. The process is highly temperature dependent and influences strongly the mechanical, thermal and chemical properties.

Due to increasing demand, over the last years considerable effort was made to develop three-dimensional constitutive models that account for a time- or degree of cure dependence of the mechanical properties. Several suggestions for simulation of polymer curing on the basis of a physically and chemically sound approach have been presented by (Adolf et al., 2004). Furthermore, both geometrically linear (Adolf and Chambers, 1997; Adolf et al., 1998; Hossain et al., 2009b) and nonlinear constitutive models have been proposed by Adolf and Chambers (1997), Adolf et al. (1998) and Hossain et al. (2009b) as well as Adolf and Chambers (2007), Adolf et al. (2004) and Hossain et al. (2009a), respectively.

Concerning the cure dependence of physical constants, several ad hoc assumptions are made in the literature. E.g. for the bulk compression modulus at least two conceptions can be distinguished: According to Meuwissen et al. (2004) a linear relationship for the bulk moduli of the monomer (or uncured resin and curing agent) and the solid is assumed which essentially represents a Voigt bound. Contrary, in Mahnken (2013) a linear relationship is obtained for the bulk compression modulus which essentially represents a Reuss bound for the inverse of the bulk modulus. Alternatively, in O'Brien et al. (2001) the bulk compression modulus is obtained from the cure dependent shear modulus by keeping Poissons's ratio constant, see also Hossain et al. (2009b). Furthermore, Mahnken (2013) derives the bulk heat-dilatation coefficient dependent on curing, whereas the bulk shrinking-dilatation coefficient is not dependent on the degree of cure. These derivations are in agreement with ad hoc assumptions by Ruiz and Trochu (2005) and Hill et al. (1995).

The above approaches have in common, that they are valid for homogeneous mixtures. In order to represent the matrix of a fibre reinforced composite on the mesoscale as an effective medium, in this work a heterogeneous microscopic configuration is used considering a representative unit cell (micro-RVE) on the microscale within a geometrical arrangement. The uncured resin, curing agent and solidified material are considered as isotropic, multi-layered concentric spherical inclusions, where the core sphere consists of the solid material. This geometrical arrangement coincides basically with the *(three phase) composite spheres*

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model in the original works of Kerner (1956), Hashin (2011), Christensen (1979) and Christensen and Lo (1979), where effective elastic moduli are derived self-consistently as exact, analytical solutions. Following on from these works, micromechanical modeling for *effective compression modulus* and *effective shear modulus* using the *n-layered composite spheres model* was introduced by Herve and Zaoui (1993). In the derivation the authors distinguish between two different approaches which yield equivalent formulations for the effective properties: the so called *stress* and the so called *displacement approach*. For the latter case, extension to pure heat-dilatation is proposed by Gusev (2014), who also provides a numerical validation with the finite element method.

This work addresses the derivation of effective material properties for the mesostructure. To this end two different conceptions are presented:

- Homogeneous matrix: An equally distributed mixture on the microscale is assumed for the three constituents which yield bounds for the meso bulk properties. In particular we derive the *bulk compression modulus* and the *bulk heat-dilatation coefficient* in dependence on the degree of cure as well as the shrinking-dilatation coefficient which is not dependent on curing. The properties are in agreement with ad hoc assumptions from the literature, i.e. the *bulk curing-dilatation coefficient* corresponds to the derivations by Hill et al. (1995), whereas the *bulk compression modulus* and the *bulk heat-dilatation coefficient* coincide with the well known lower Reuss bounds. Thus, we combine these formulations for the volumetric quantities to a model which we denote as the Reuss model. For completion we also introduce a so called Voigt model which includes upper Voigt bounds for the bulk compression modulus and the bulk heat-dilatation coefficient. It shares the *bulk curing-dilatation coefficient* with the Reuss model, as it is constant during curing.
- Heterogeneous matrix: An arrangement of a heterogeneous microstructure is taken into account. Thus, our work represents an extension of the *composite spheres model* by Christensen et al., where in addition to the *effective compression modulus* it includes also thermal and chemical effects. As we restrict to thermo-chemo-linear elasticity for simplification, the *effective compression modulus*, the *effective bulk heat-* and the *effective bulk curing-dilatation coefficients* are provided applying the *stress approach*, cf. Herve and Zaoui (1993), as analytical solutions for the micro-RVE which is contrary to the bounds for the homogeneous mixture. To the authors best knowledge, the derivation for the *effective bulk curing-dilatation coefficient* has not been proposed previously in the literature, whereas the formulation in our work for *effective heat-dilatation coefficient* is equivalent to the derivations by Gusev (2014) who applies the *displacement approach*. The agreement of the effective bulk quantities in our work with those from the literature is highlighted.

The organization of this paper is summarized as follows: Section 2 introduces the preliminaries for two reaction mechanisms for thermosetting polymers and presents a three-scale framework for fibre reinforced polymer curing. We introduce the meso-RVE consisting of a matrix and a fibre part. Furthermore, three phases of the polymeric matrix are defined and thus, mass phase fractions are introduced to derive bulk material parameters for the mesoscopic behavior. Based on these preliminaries, two conceptions are distinguished: Firstly, in Section 3 an equally distributed mixture on the microscale is assumed, secondly, in Section 4 an arrangement of a heterogeneous microstructure is taken into account. In Section 5 we compare the meso-micro relations for the homogeneous matrix which yield (upper) Voigt and (lower) Reuss bounds with those derived for the heterogeneous matrix which yield effective parameters. Elastic, thermal and chemical material properties are compared versus the degree of cure.

Notations

Square brackets [•] are used throughout the paper to denote ‘function of’ in order to distinguish from mathematical groupings with parenthesis (•).

2. Preliminaries for the curing of thermosetting polymers

2.1. Polymerization mechanisms

Epoxy resin systems are included in the group of thermosetting polymers (thermosets). Starting with the initial uncured state the matrix (a mixture of resin and curing agent) undergoes a polymerization process during curing. As introduced by Flory (1953) two polymerization reaction mechanisms are distinguished 1. by free-radicals or ions (*chain-growth polymerization*) and 2. by functional groups (*step-growth polymerization*).

Considering the scheme of *chain-growth polymerization* shown in Fig. 1a starting with an initiator the unsaturated monomer molecules add onto the active site of a growing polymer chain one at a time. Different steps operate at different stages of the mechanism (i.e. initiation, propagation, termination, and chain transfer). Following Cowie and Arrighi (2007), the characteristics of *step-growth polymerization* are the growth throughout the matrix, whereas no initiator is necessary and the reaction between any two functional groups of monomers is stepwise. Thus, at multiple locations and at the same time similar steps are repeated throughout the reaction process as illustrated in Fig. 1b. In particular initiation, propagation and termination reactions are essentially identical in rate and mechanism as shown Fig. 1c. Therefore, the chain length increases steadily and random growth takes place as the monomer reacts with both monomer and polymer species with equal ease as described in Stille (2005): “Thus, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer. This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time, a high molecular weight polymer is obtained.” All in all, with evolving curing polymer chains form and cross-link to each other resulting in a three dimensional network such that the viscosity of the liquid resin, its molecular weight and the stiffness increase, whereas the rate of increase is dependent on the reaction mechanism. The process is highly temperature dependent and influences strongly the mechanical, thermal and chemical properties.

Taking into account both reactions mechanism is the decisive point for two conceptions for the matrix (the *homogeneous matrix* and the *heterogeneous matrix*) we distinguish later on. Especially for the *step-growth polymerization* we assume an idealization: For the locations from where on random growth starts we assume a probabilistic distribution. The random growth is then represented by multiple growing spherical inclusions with its origins at those multiple locations from where on the molecular functional groups of monomers start to react, i.e. the phase of cross-linked monomers in Fig. 1c at one of the multiple locations in Fig. 1b. This region is surrounded by a phase including mainly monomers.

2.2. A three-scale framework for fibre reinforced polymer curing

Based on the polymerization mechanisms described in the previous subsection Fig. 2 gives an overview of the three-scale framework. $\bar{\Pi} \subset \mathcal{R}^3$ denotes the homogeneous macrostructure. It

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