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Thermo-chemo-mechanical effective properties for homogeneous and heterogeneous *n*-phase mixtures with application to curing

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Abstract

Our work presents an extension of a composite sphere model to temperature-dependent elastic effects accompanied by curing. Homogenization of a representative unit cell (micro-RVE) on the heterogeneous microscale which accounts for thermo-chemo-mechanical coupling with linear elasticity yields volumetric effective properties. Two conceptions are considered: Firstly, a homogeneous mixture with *n*-phases is assumed. Secondly, a geometric arrangement on the microscale is represented by the *n*-layered composite sphere model. In a numerical study for a 3-phase matrix it is demonstrated that the effective properties lie within certain bounds.

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1. Introduction

Polymeric materials are broadly applied in carbon- and glass fibre-reinforced composites (FRP), epoxy laminates and particle-reinforced polymer structures, cf. [1], [2]. Two important production processes of FRPs are resin transfer molding (RTM) and reaction injection molding (RIM). In both processes a fibre preform or dry fibre reinforcement is packed into a mold cavity. After closing, a resin or resin system as mixture of reactants, e.g. resin and curing agent, is pumped into the mold under pressure until the mold is filled. Subsequently the curing cycle starts.

A reliable and predictive simulation of the production process requires the thermo-chemo-mechanical effective material properties depending on curing. For this purpose homogeneous and heterogeneous conceptions for the matrix can be distinguished as follows:

- Homogeneous mixture: An equally distributed mixture is assumed for all constituents, resin, curing agent and solidified material. Concerning the cure dependence of *effective properties*, several ad hoc assumptions are made in the literature. At least two approaches can be distinguished for the effective properties, e.g. for the compression modulus: According to [3] a linear relationship is assumed for the compression moduli of the monomer (or uncured resin and curing agent) and the solid which essentially represents an upper Voigt bound. Contrary, in [4] a linear relationship is derived for the effective compressibility which essentially represents a lower Reuss bound for the effective compression modulus. It is well known, that the effective properties obtained for a homogeneous mixture are only dependent on phase fractions. These are bounds for more advanced approaches, where a geometrical arrangement of the heterogeneous microscale is taken into account.

- Heterogeneous mixture: A geometrical arrangement of a heterogeneous microstructure is introduced in [6] in a so called *composite sphere*

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model. To solve for effective properties as exact, analytical solutions for a *2-layered composite sphere model*, a 2-layered inclusion is compared to an *equivalent homogeneous sphere* with identical boundary conditions, see [7]. Concerning the cure dependence of the effective properties, in [8] the 2-layered composite sphere model is extended to account for thermo-chemo-mechanical coupling. In [9], a mesoscopic model for temperature-dependent visco-elastic effects accompanied by curing of FRP is investigated. In comparison to Voigt and Reuss bounds, the effective properties from [8] for a 2-phase mixture are used. The authors conclude, that the eigenstrain state for a fully cured FRP is strongly dependent on the choice of effective properties. Based on the works [6], [7], micromechanical modeling for the effective elastic moduli for an n-layered spherical inclusion is introduced in a so called *$(n+1)$-phase model* in [10]. Here, an infinite medium is constituted of an n-layered inclusion, embedded in a matrix which is denoted by phase $n+1$. An extension of an n-layered composite sphere model to pure heat-dilatation is proposed by [11]. Furthermore, for the $(n+1)$-phase model a thermo-chemo-mechanical coupling is proposed in [12], where it is also shown that the n-layered composite sphere model and the $(n+1)$-phase model yield identical results.

To the authors knowledge, all three constituents, resin, curing agent and solid, occurring in the curing process (of a polymeric matrix) have not been considered so far by a 3-layered composite sphere model to derive volumetric effective properties while accounting for thermo-chemo-mechanical coupling. This contribution aims to close this gap. In order to become more general, the case with n spherical constituents is taken into account. To this end, two different conceptions are investigated: Firstly, an equally distributed n-phase *homogeneous mixture* is assumed on the microscale. Secondly, an extension of the 2-layered composite sphere model in [8] an n-layered composite sphere is considered on the microscale as a *heterogeneous mixture*.

2. Composite sphere models: Overview

Figure 1 introduces two different idealizations which are used for the derivation of effective properties in the following sections: a) a homogeneous mixture and b) an n-layered composite sphere model as extension of [7]. Both idealizations have in common that a *spherical inclusion* is embedded in an infinite homogeneous medium which following [10] is denoted as *matrix*. Both are subjected to

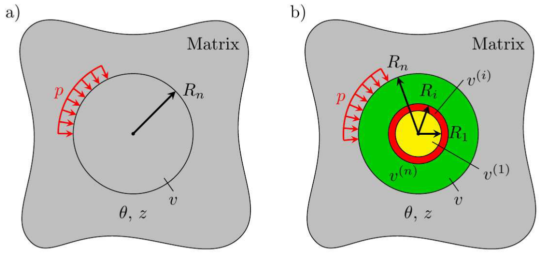

Fig. 1: Two idealizations of the inclusion: a) homogeneous sphere *hom*, b) heterogeneous n-layered composite sphere *het*$[n]$.

a uniform thermal loading in terms of a prescribed temperature θ and a chemical loading in terms of a degree of cure z (of a thermosetting polymer as in [8]). In addition, the inclusion is subjected to mechanical loading in terms of a prescribed pressure p. The distinguishing features of both conceptions in Figure 1 are as follows:

a) Homogeneous mixture: Any spherical inclusion with total volume v and radius R_n is homogeneous and represents the effective behavior.

b) n-layered composite sphere model: The constituents $i \in [1, n]$ with partial volumes $v^{(i)}$ (that is for $n = 3$ from inside to outside: solid (*sol*), curing agent (*ca*), resin (*r*)) and corresponding radii R_i assemble to a total volume v.

3. Homogeneous mixture: *n*-phase homogeneous matrix model

In this section, we summarize the results in [4] for weighted effective properties of a 3-phase homogeneous mixture and apply it to the matrix shown Figure 1.a which consists of phases $i \in [1, n]$. At any material point P within the inclusion, $dm^{(i)}[t]$ defines the time dependent mass of a constituent $i \in [1, n]$ and dm_0 is the total mass of the mixture which is conserved during the curing reaction, cf. [13]. With this quantities we define the mass fraction of each constituent $\zeta^{(i)}[t] = \frac{dm^{(i)}[t]}{dm_0} \geq 0$ which is used to formulate the mixture rule for the inverse of the bulk density ρ

$$1.\ \frac{1}{\rho} = \sum_{i=1}^{n} \frac{\zeta^{(i)}}{\rho^{(i)}}, \quad \text{where} \ \ 2.\ \rho^{(i)} = \rho^{(i)}[p, \theta]. \qquad (1)$$

Using the assumption that all phases are equally distributed, the number of variables can be reduced by taking into account the stoichiometry of the mixture, as explained in [13]. To this end, the *degree of cure* $0 \leq z[t] \leq 1$ is introduced which represents the chemical loading in Figure 1.a resulting in the relation $\zeta^{(i)} = \zeta^{(i)}[z]$ for the mass fractions in Eq. (1.1). Combining this with Eq. (1.2) implies that