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Using a pattern-based homogenization scheme for modeling the linear viscoelasticity of nano-reinforced polymers with an interphase

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The self-consistent model based on morphological representative patterns is applied to the realistic case of the linear viscoelasticity of polymers reinforced by elastic nano-particles coated with a viscoelastic interphase. This approach allows to study the effect of such microstructure parameters as particle dispersion, particle size distribution and interparticle distance distribution. Under the assumption that the interphase has the same thickness around all reinforcing particles, it is shown that the particle size distribution has little effect on the effective properties of the heterogeneous material, whereas the particle dispersion and the interparticle distance distribution have stronger impacts.

1. Introduction

Few studies have investigated the interest of the morphological representative pattern (MRP) approach introduced by Stolz and Zaoui (1991) and which defines a micromechanics framework that accounts for the microstructure characteristics of materials. Bornert (1996) has included the MRP approach in a self-consistent scheme which has been applied mainly by this author and his co-workers. For instance, Bilger et al. (2007) used this self-consistent scheme to study the effect of a non-uniform void distribution in porous materials and Chabert et al. (2004) applied it to viscoelastic polymers reinforced by silica, but without accounting for a possible material interphase or for particle size distributions.

Taking an interphase into account in various materials has been performed by using the 4-phase self-consistent model in many papers. This model is based on a 3-phase spherical inclusion embedded in the homogeneous equivalent medium and has been given with full details by Maurer (1990), with applications to interphases in viscoelastic materials by Maurer (1986), Schaeffer et al. (1993), Eklind and Maurer (1996), Colombini et al. (1999), Reynaud et al. (2001), Colombini et al. (2001), Colombini and Maurer (2002), among others. A derivation of the same model leading to different equations, has also been proposed by Hashin and Monteiro (2002), for an interphase problem in elastic materials.

In a recent work (Diani et al., 2013), the present authors studied the viscoelastic behavior of several carbon-black filled styrene butadiene rubbers (SBRs). The experimental data showed evidences in favor of the existence of an interphase at the rubber–filler interface, with enhanced viscoelastic properties compared to the bulk matrix viscoelasticity. The behavior and the thickness of the interphase were estimated by using the 4-phase self-consistent model, which allowed a very good prediction of the viscoelastic behavior of several filled SBRs, but the interphase thickness was estimated to an arguably large

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value of 5 nm for spherical particles with a radius of 30 nm. Therefore, it seemed interesting to apply a more elaborate model that allows for the introduction of more microstructure parameters, and to see how the evaluation of the interphase thickness evolves. With the MRP approach, one may study the effect of parameters such as particle dispersion, particle size distribution and interparticle distance distribution. The method is applied here to one of the above-mentioned carbon-black filled rubbers, where the carbon-black agglomerates are approximated by elastic spherical particles, and where both the polymer interphase and the polymer matrix are viscoelastic. The mechanical behaviors considered for the constitutive phases are realistic, and therefore the homogeneous equivalent medium can be compared to the behavior of an actual carbon-black filled SBR. Considering actual materials gives a sound framework to study the impact of some of the parameters used in the MRP approach.

The paper is organized as follows. In the next section, the general equations of the MRP self-consistent model are detailed in a comprehensive and an easy way, in order to favor its use among the scientific community. Additional equations that are useful for the specific case of 3-phase spherical patterns are also detailed, and the model parameters are discussed. Then, the effects of particle dispersion, particle size distribution (based on realistic carbon-black filler distributions), and interparticle distance distribution on the predicted viscoelastic behavior of the heterogeneous material are examined by accounting for a large number of patterns. The comparison between the model predictions and the behavior of an actual filled rubber provides estimates for the interphase thickness according to the microstructures considered.

2. Morphologically representative pattern-based self-consistent model

2.1. General theory

The main motivation of the MRP self-consistent model introduced by Bornert (1996) is to account for some dispersion and size effects that cannot be included in classical homogenization schemes. Given a schematic representation of a material reinforced by randomly distributed particles of various sizes and geometries (Fig. 1), the idea is to recognize the various patterns that are found within the material (Fig. 2) and to build a homogenization scheme that takes them into account.

Let us assume that the heterogeneous material contains p constitutive phases with volume fractions f_j and elastic stiffness tensors $\boldsymbol{C}_j$, $j \in \{1, 2, \ldots p\}$. The objective of any homogenization scheme is to compute the behavior $\boldsymbol{C}_h$ of the homogeneous equivalent medium (HEM) defined by

$$\boldsymbol{C}_h = \sum_j f_j \, \boldsymbol{C}_j : \boldsymbol{A}_j \tag{1}$$

where the average strain localization tensor $\boldsymbol{A}_j$ in phase j is given by

$$\bar{\epsilon}_j = \boldsymbol{A}_j : \boldsymbol{E} \tag{2}$$

where $\bar{\epsilon}_j$ is the average strain in phase j and $\boldsymbol{E}$ is the overall strain applied to the heterogeneous material that may be written as

$$\boldsymbol{E} = \sum_j f_j \, \bar{\boldsymbol{\epsilon}}_{\boldsymbol{j}}. \tag{3}$$

Let us account now for the description of the heterogeneous material as a perfectly disordered distribution of patterns of n different types, plus a complement of matrix material left between the patterns, as shown in Fig. 2. The latter residual matrix volume has no specific shape, but it is treated as a single spherical homogeneous pattern Ω_0 because of its statistically isotropic distribution over the heterogeneous material, as done in the Hashin and Shtrikman (1963) approach for bounds. This differs from the spherical shape used for the other patterns, which originates from the actual shape of the particles. In general, several copies of each Ω_λ pattern ($\lambda > 0$) are present in the heterogeneous medium, but considering a single copy is sufficient in a self-consistent model, where any pattern is assumed to behave as if surrounded by the

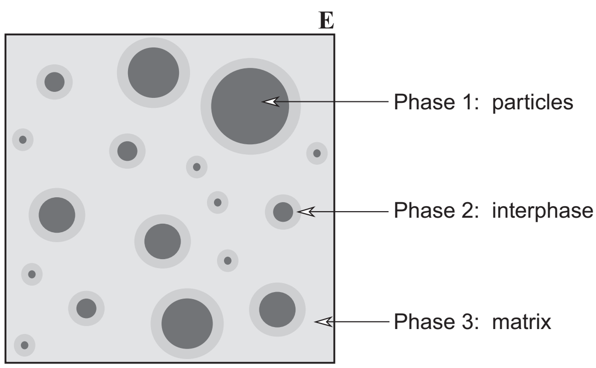

Fig. 1. Schematic representation of a material reinforced by randomly distributed particles of various sizes and coated with an interphase.