Dynamic moduli of filled elastomers – A coarse grained computer model

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A coarse grained computer model is presented in the context of dynamic mechanical analysis of filled elastomer networks. The model relates both storage and loss modulus as functions of shear frequency and strain amplitude to filler content and structure as well as to parameters describing matrix–filler and filler–filler interaction on the nano-scale. We show how such a coarse grained model may be used to guide the developer of filled elastomer applications in the understanding of the interplay between molecular interface design and macroscopic performance with respect to the Payne effect.

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1. Introduction

Dynamic moduli as functions of amplitude, frequency or temperature are essential data for the developer of filled rubber applications [1–7] especially in the automotive industry. Dynamical mechanical analysis is one of the major experimental techniques by which to gauge the technical performance of filled rubbers or elastomers. It is well known that the technical performance of filled rubbers is strongly influenced by the molecular details of the interfaces between the components (for a recent review see [8])-here we refer in particular to three components: rubber, filler, and, if applicable, coupling agent. A primary goal in this field is the prediction and tuning of macroscopic performance on the basis of molecular interactions and molecular engineering. Unfortunately, no experimental technique allows direct observation of the relevant interfaces on the molecular scale as does for instance scanning probe microscopy at solid–gas or solid–liquid interfaces. Probably because of the lack of direct probes the physics and chemistry of the above interfaces continue to be areas of basic research driven by the economic relevance of filled rubber products.

On the theoretical side scientific computing has become a powerful tool. However, it still is impossible to perform molecular simulations allowing virtual mechanical testing and simultaneous observation of the underlying dissipative molecular processes. One should bear in mind that a typical primary filler particle may posses 10^4 to 10^5 'anchoring sites' on its surface responsible for the interaction with the rubber matrix. Thus it is impossible to include both a reasonable number of primary filler particles, reasonable in the sense that the macroscopic filler distribution is well represented, and molecular detail of the aforementioned interfaces into a single molecular simulation. Nevertheless, it has been tried to compromise between system size and the neglect of detail. An example is Ref. [9], where the authors study the role of particle–particle interaction. Here much of the chemical detail of the polymer matrix is retained. But consequently the number as well as the relative size of the filler particles is exceedingly small.

The opposite limit, i.e. the computational investigation of the filled rubber product as a whole and under realistic operating conditions, is dominated by the finite element method (FEM). FEM is applied to the solution of partial differential equations derived from the theory of elasticity

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and/or other continuum theories describing the system of interest in terms of material parameters, e.g. elastic constants, equilibrium thermodynamic parameters, and transport coefficients, as input together with appropriate boundary conditions. The trouble here is that physical and chemical modification of the interfaces between the components, which are largely responsible for the performance, are localized on the nm-scale. This scale only is accessible to this approach if one is willing to surrender the ability to model the macroscopic system. But one must be aware that the continuum limit, even though it often holds down to almost molecular dimensions, fails eventually when molecular dimensions are approached. Nevertheless, Gusev [10] has carried out an interesting study of the micro mechanical mechanism of reinforcement and loss in filled rubbers along these lines, albeit on a very small system. He studies periodic cells containing 8 silica spheres at a volume fraction of about 0.32. He finds both a pronounced increase of reinforcement and loss due to the presence of a 'glassy layer' surrounding the filler. It is important to note that this conclusion rests on a priori assuming a strong stiffness of the glassy layers compared to the rubber matrix. However, little is known about the true nature of the glassy layer [11].

In the following we develop a coarse grained model conceptually related to previous models by Long, Sotta and coworkers [14,15] (and references therein). The main finding of these authors again is the pronounced strengthening when glassy layers overlap. Instead of focussing on the glassy layer as such, or more precisely the interaction between filler particles, we explicitly include the rubber–filler interface. This enables us to study the 'competition' between rubber–filler and filler–filler interfaces. In our model interactions and interfaces between the components, i.e. rubber, filler, and coupling agent, are represented by phenomenological potentials containing parameters, which may be adjusted to reproduce interfacial properties on the nm-or even sub-nm-scale. The idea is to relate parameter changes in the different interfaces to molecular modifications of the latter and to tie these to changes of the dynamic moduli in specific frequency, amplitude, and possibly temperature ranges. The developer would thus be given useful guidance when tuning macroscopic properties of filled rubber products through chemical and physical modification of the attendant interfaces. In addition the model enables us to illuminate effects linked to the filler concentration as well as its spatial filler distribution (random, fractal, etc.).

In the present work our main focus is the dependence of the storage modulus, μ', and the loss modulus, μ'', including related quantities like $\tan \delta = \mu''/\mu'$ and the magnitude of the complex modulus, $|\mu^*|$, on shear frequency and strain amplitude. We show that our model reproduces important features of the strain amplitude dependence for filled rubbers. In particular it relates the Payne effect to the aforementioned interaction parameters allowing to discriminate between contributions associated with loss processes in the different interfaces. We note that the relative importance of loss processes in the rubber–filler vs. the filler–filler interface as primary source of the Payne effect is still debated in the literature [6,16,17].

The paper is structured as follows. The subsequent section introduces the model and its relation to experimental dynamic mechanical measurements. Section 3 presents specific results. First we study the dependence of the moduli on frequency when no filler is present. Subsequently we study the same dependence as well as the dependence on amplitude in the presence of randomly distributed filler. In particular we investigate and discuss the dependence of the Payne effect on the interaction parameters in the model. Section 4 is the conclusion. In an appendix we explain how the current concept may be extended to include real time as well as temperature.

2. Methodology

Our basic approach is derived from atomistic modeling, i.e. we do not discretize a continuum description resulting in certain partial differential equations describing filled elastomers. Likewise our solution method is derived from iterative solution schemes used in atomistic modeling rather than being a finite volume, finite difference or finite element method. A pictorial example of our model is shown in Fig. 1. A close to cubic volume containing the rubber–filler network is divided into volume elements or nodes on a fcc-lattice (other lattice types are possible also). Each node represents either a rubber volume element or a primary filler particle. Even though the concept of a 'primary particle' eventually must be replaced by appropriate aggregates/agglomerates, at this point it is a useful basis. The distance between nearest-neighbor nodes is D, the diameter of a primary filler particle, which sets the unit of length. The model thus allows variation of filler content, its distribution structure, and the details of the interactions between adjacent nodes as explained below. We emphasize that the filler distribution is fixed, i.e. as in technical applications, where the filler distribution is due to the mixing process and unchanged thereafter, do the filler particles move in response to external forces but do not "diffuse" in any way. The model's output consists of storage and loss modulus as functions of the aforementioned variables including frequency and amplitude of a periodic
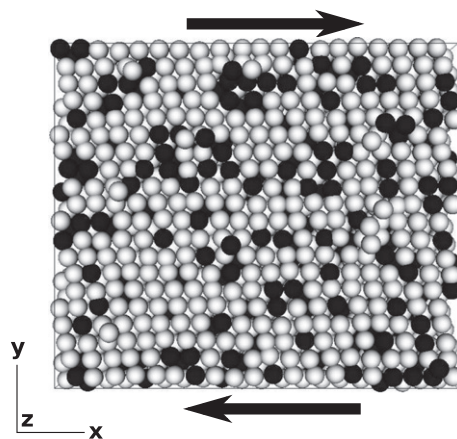

Fig. 1. A $20 \times 20 \times 20$ fcc lattice system with 20% filler (black spheres) content and at 30% shear amplitude.