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Microstructure-based modelling of arbitrary deformation histories of filler-reinforced elastomers

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A B S T R A C T

A physically motivated theory of rubber reinforcement based on filler cluster mechanics is presented considering the mechanical behaviour of quasi-statically loaded elastomeric materials subjected to arbitrary deformation histories. This represents an extension of a previously introduced model describing filler induced stress softening and hysteresis of highly strained elastomers. These effects are referred to the hydrodynamic reinforcement of rubber elasticity due to strain amplification by stiff filler clusters and cyclic breakdown and re-aggregation (healing) of softer, already damaged filler clusters. The theory is first developed for the special case of outer stress–strain cycles with successively increasing maximum strain. In this more simple case, all soft clusters are broken at the turning points of the cycle and the mechanical energy stored in the strained clusters is completely dissipated, i.e. only irreversible stress contributions result. Nevertheless, the description of outer cycles involves already all material parameters of the theory and hence they can be used for a fitting procedure. In the general case of an arbitrary deformation history, the cluster mechanics of the material is complicated due to the fact that not all soft clusters are broken at the turning points of a cycle. For that reason additional reversible stress contributions considering the relaxation of clusters upon retraction have to be taken into account for the description of inner cycles. A special recursive algorithm is developed constituting a frame of the mechanical response of encapsulated inner cycles. Simulation and measurement are found to be in fair agreement for CB and silica filled SBR/BR and EPDM samples, loaded in compression and tension along various deformation histories.

1. Introduction

Reinforcement of polymer networks by nano-structured fillers like carbon black or silica plays an important role in the improvement of wear and fatigue of elastomer products. The use of fillers together with accelerated sulphur vulcanisation has remained the fundamental technique for achieving the incredible range of mechanical properties required for a great variety of modern rubber products. However, besides making the elastomer stiffer and tougher, the incorporation of a filler brings about a non-linear dynamic-mechanical response reflected by the amplitude dependence of the dynamic moduli. This effect was investigated by several authors like Payne (1963, 1964), Kraus (1965) and Medalia (1973, 1978). A related phenomenon is the stress softening effect under quasi-static cyclic deformation, which was studied intensively by Mullins and co-workers (Mullins and Tobin, 1965) and other authors (Kraus, 1965). Dependent on the history of straining, e.g. the

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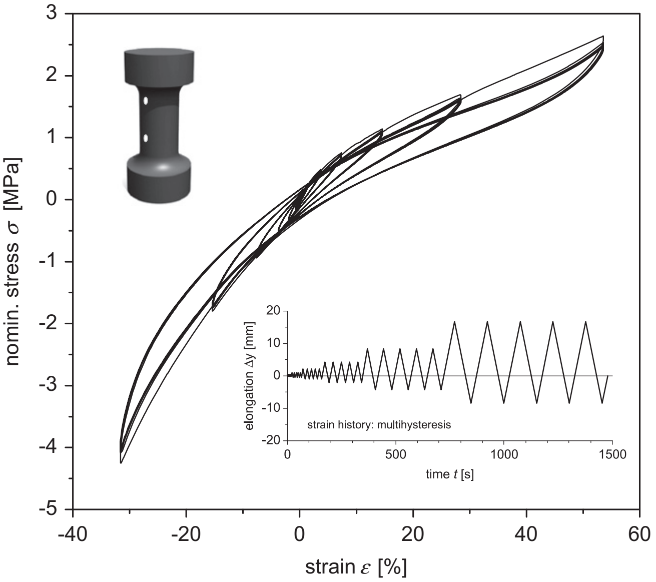

Fig. 1. Uniaxial stress–strain cycles measured with dumbbells in tension–compression mode for successively increasing strain of a carbon black filled S-SBR/BR rubber blend (60 phr N339) demonstrating the typical stress softening effect. The inset shows the strain history.

extent of previous stretching, the rubber material shows an almost permanent damage of the internal structure implying that the elastic response becomes significantly softer. Most of the stress softening occurs in the first cycle, and in the following cycles the specimen approaches a steady state stress–strain curve. An example for a carbon black filled S-SBR/BR blend is depicted in Fig. 1. A second characteristic effect caused by fillers is the pronounced increase of the hysteresis which is related to the dissipation of mechanical energy. All these effects are temperature- and time-dependent and are interrelated due to their common origin. But, neither the elastomer nor the pure filler alone shows such behaviour. The filler is composed of relatively stiff particles that do not undergo significant deformation by themselves. During the vulcanisation (heat treatment) of rubber, filler particles form clusters. This process represents a form of diffusion-controlled aggregation and is also called flocculation. The resulting filler structure determines the mechanical behaviour. On the other hand, the entropy-elastic behaviour of the elastomer or rubber matrix is well understood and may be described e.g. by the extended non-affine tube model (Heinrich et al., 1988; Klüppel and Schramm, 2000).

The micro-mechanical origin of the stress–strain behaviour of filled elastomers, as depicted e.g. in Fig. 1, has been formulated in the Dynamic Flocculation Model (DFM) and identified in a dynamic creation and damage of filler–filler bonds, i.e. glassy-like polymer bridges of some nanometres in width between adjacent filler particles (Klüppel and Meier, 2001; Klüppel, 2003; Klüppel et al., 2005). This thermodynamically irreversible process leads to a dissipation of mechanical energy and has analogies to the action of frictional forces. The damage of bonds is structurally reversible, which means that re-aggregation of filler particles takes place upon retraction. However, the re-aggregated bonds differ from the initial ones in stiffness and strength, which can be considered as the main reason for stress softening and filler-induced hysteresis. Stress softening has also been treated on a phenomenological level by assuming a multiplicative decomposition into elastic and plastic components (Govindarajan et al., 2008). The close relation between the quasi-static stress softening (Mullins effect) and the drop of the modulus with increasing dynamic strain amplitude (Payne effect) becomes apparent in the consideration of the non-linear viscoelastic response of filled rubbers by the statistical hyper-visco-elastic–plastic model proposed by Boukamel et al. (2005, 2008). An alternative micro-mechanical approach explains the Mullins effect of filled elastomers by a stress-induced irreversible slippage of polymer chains across the filler surface (Dannenber, 1975; Govindjee and Simo, 1991, 1992). A related model has been proposed by Maier and Göritz (1996) to explain the Payne effect by a cyclic detachment and re-adsorption of chains from the filler surface under harmonic strain. But, not much definitive can be said, except that an instable mechanical behaviour at the polymer filler interface results in a very localised deformation in thermodynamic non-equilibrium.

In this context it is important to note, that the structure of the filler within the matrix is responsible for the mechanical reinforcement and stress–strain relation (Huber, 1997; Huber and Vilgis, 1999; Klüppel and Heinrich, 1995; Klüppel et al., 1997; Heinrich and Klüppel, 2002). A steady-state stress–strain cycle results, when the same amount of bonds is damaged and recovered during a cycle. This was already part of an empirical approach by Kraus (1984), but it did not permit any relation to the real microstructure and its universal properties. If the filler volume fraction in a rubber compound goes beyond a critical value, a percolated filler network is formed. But, already under low deformations this network starts to break down, and the storage modulus drops from relatively high to low values. This makes clear, that not only the mere