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A constitutive model for the Mullins effect with permanent set in particle-reinforced rubber

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Abstract

Stress softening during initial loading cycles, known as the Mullins effect, and the residual strain upon unloading are not accounted for when the mechanical properties of rubber are represented in terms of a strain-energy function, i.e. if the material is modelled as hyperelastic. In this paper we first describe some experimental results that illustrate stress softening in particle-reinforced rubber together with associated residual strain effects. In particular, the results show how the stress softening and residual strain change with the magnitude of the applied strain. Then, on the basis of these data a constitutive model is derived to describe this behaviour. The theory of *pseudo-elasticity* is used for this model, the basis of which is the inclusion of two variables in the energy function in order separately to capture the stress softening and residual strain effects. The dissipation of energy, i.e. the difference between the energy input during loading and the energy returned on unloading is also accounted for in the model by the use of a *dissipation function*, which evolves with the deformation history.

Keywords: Pseudo-elasticity; Particle-reinforced rubber; Dissipation function; Mullins effect

1. Introduction

This study is concerned with the formulation of a constitutive model to capture certain inelastic effects in particle-reinforced rubbers subjected to uniaxial loading–unloading cycles in tension. As a basis for the modelling we use some recently obtained experimental data. The effects of strain history on the stresses and the formulation of constitutive models for filled and unfilled elastomers have been a particular focus of attention during the last few years. This is evidenced by the large number of recent publications, representative examples being the papers by Govindjee and Simo (1991, 1992a,b), Johnson and Beatty (1993, 1995), Lion (1996, 1997), Papoulia and Kelly (1997), Kaliske and Rothert (1998), Reese and Govindjee (1998), Septanika and Ernst (1998), Ogden and Roxburgh (1999a,b), Miehe and Keck (2000), Beatty and

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Krishnaswamy (2000), Meisner and Matějka (2000, 2001) and Dorfmann et al. (2002). Valuable sources of references are also contained in the collections of papers from the proceedings of the first two European Conferences on Constitutive Models for Rubber edited by Dorfmann and Muhr (1999) and Besdo et al. (2001). This interest has been generated and maintained by the increasing industrial use of carbon black (CB) filled elastomers, for example in vibration isolators, earthquake bearings, seals and flexible joints in addition to extensive use in vehicle tires. Accidents caused by the failure of components made of CB-filled elastomers, for example the explosion of the space shuttle Challenger in 1986 or the recent well-publicized failure of the Firestone ATX/AT tires, has brought to light the need for a better understanding of the basic physical properties of these materials and the possible causes of failure. Pre-requisites for this understanding are suitable experimental data and a good constitutive model for the material behavior.

Particle-reinforced rubbers exhibit a marked hysteretic response during unloading after loading in uniaxial tension, compression or shear, for example, i.e. the stress on unloading is significantly less than that on loading at the same strain. The difference in the stresses corresponding to the same strain level under loading and retraction depends primarily on the proportion of filler in the rubber compound; for unfilled rubber the difference is negligible but it becomes very marked for elastomers with a high CB content. The stress difference is greatest during the first loading–unloading cycle and approaches a fixed (strain-dependent) value after a number of cycles. For more details we refer to, for example, Lion (1996) and the references therein.

When an unfilled or CB-reinforced rubber is subjected to cyclic loading with a fixed amplitude in simple tension, compression (Bergström and Boyce, 1998) or shear (Ernst and Septanika, 1999; Sedlan, 2000) from its initial (virgin) natural configuration, the stress required on reloading is less than that on the initial loading for elongations up to the maximum elongation achieved. The stress differences in successive loading cycles are largest during the first and second cycles and becomes negligible after about 6–10 cycles, depending on the amount of filler and maximum extension. Experimental results illustrating this phenomenon for both unfilled and particle-reinforced rubber were first published in a series of papers by Mullins and co-workers starting in the late 1940's and became known as the Mullins effect (Mullins, 1947, 1969; Mullins and Tobin, 1957, 1965; Harwood et al., 1965; Harwood and Payne, 1966a,b, 1967). Different micro-mechanical interpretations have been provided in order to explain the softening phenomenon. The observed stiffness reduction was initially attributed solely to the rupture of filler clusters and to the separation of weak polymer chains from the fine particle fillers. However, the concept of rubber-filler interaction is not on its own sufficient to explain this phenomenon since the effect is present in unfilled as well as reinforced elastomers. Other micro-mechanical interpretations have been provided in order to explain this effect; for example, the untangling or breakage of weak crosslinks in unfilled rubber or different forms of separation of weak bonds between filler particles and long chains in filled rubber. A selection of the large number of works published on this topic are the papers by Bueche (1960, 1961), Bonart (1968), Dannenberg (1974), Rigbi (1980), Lee and William (1985), Roland (1989a,b,c), Muhr et al. (1999), Krishnaswamy and Beatty (2000), DeSimone et al. (2001), Drozdov and Dorfmann (2001) and Marckmann et al. (2002).

A CB-filled rubber after loading and subsequent unloading does not in general return to its initial state corresponding to the natural stress-free configuration, but exhibits a residual strain or permanent set (which slowly decreases in time and essentially disappears after a sufficiently large period of annealing). The magnitude of the residual strain depends on the amount of CB in the rubber and on the maximum elongation of the rubber specimen prior to unloading. For unfilled rubber the magnitude of the residual strain is negligible; however, for filled compounds it is significant and increases with the CB filler volume fraction. For series of experimental data we refer to, for example, the work of Lion (1996, 1997).

The hysteretic behaviour, the stress softening associated with the Mullins effect and the residual strain are not accounted for when the mechanical properties are represented in terms of a strain-energy function, i.e. if the material is modelled as hyperelastic. In this paper the theory of *pseudo-elasticity* due to Ogden and Roxburgh (1999a) is used to model the softening and residual strain characteristics of reinforced rubber.

It is to be recalled that the term *pseudo-elasticity* is used in the scientific literature do describe material behaviour with hysteretic characteristics, i.e. the loading–unloading response does not coincide, even though the body returns to the original state. This terminology was used, for example, by Fung (1980) to describe the response of biological tissues and by Müller (1986) to model the response of shape-memory alloys.

Ogden and Roxburgh (1999a) used a single additional (softening) variable to model the idealized Mullins effect. In the present paper the model is based on the inclusion of two additional variables in the energy function so that it is modified to capture the observed softening and residual strain response. This approach uses an internal variable, damage like approach involving specific, implicit statements for complimentary relationships. The dissipation of energy, i.e. the difference between the energy input during loading and the energy returned on unloading is accounted for in the model by the use of a *dissipation function*, which changes between unloading and subsequent reloading beyond the previous maximum strain.

The paper is organized as follows. In Section 2 we summarize experimental results for simple tension for three rubber compounds with different proportions of filler. In Section 3 we outline the required equations of nonlinear elasticity, first for general deformations and then for the appropriate pure homogeneous strain specialization. The necessary equations of pseudo-elasticity are provided in Section 4. These equations are then adapted in Section 5 in order to capture the inelastic effects of CB-reinforced rubbers. Then, in Section 6, the theory of Section 5 is used to fit the actual data. Section 7 contains some concluding remarks.

2. Experimental results

To assess the effect of stress softening and the magnitude of the accumulated residual strain in particle-reinforced rubber, several series of periodic loading–unloading uniaxial extension tests were carried out at constant temperature. Dumbbell specimens were provided by SEMPERIT (Austria). Three different natural rubber compounds were used, the first with 1 phr (by volume) of CB filler, the second with 20 phr and the third with 60 phr. A filler content of 1 phr does not affect the mechanical behaviour significantly compared with that of an unfilled rubber and can therefore be considered as essentially unfilled.

The periodic loading, unloading and reloading tests were performed using a constant strain rate of 0.02 s^{-1} at a constant temperature of 25 °C. To measure the longitudinal strain, mechanical grips, separated by an initial distance of 15 mm, were applied to the central part of each specimen before loading. Changes in the distance between these grips were measured with an accuracy of less than 3 μm. The tensile force was measured by using a standard loading cell with an accuracy of 0.05 N. The nominal stress was determined as the ratio of the axial force to the (undeformed) cross-sectional area of a specimen (2 mm × 4 mm) in the stress-free state, all specimens having the same dimensions.

During the first series of tests one specimen from each compound was subjected to six cycles of pre-conditioning up to a pre-selected extension with stretch $\lambda = 3$. The pre-conditioning was performed in order to monitor the progression of stress softening, to evaluate the accumulation of residual strain and to determine the ultimate stress-deformation response for stretches up to $\lambda = 3$. The results are reported as nominal stress versus stretch λ and are shown in Figs. 1–3. Fig. 1 shows the stress-stretch response for the natural rubber compound with 1 phr of CB. Figs. 2 and 3 show corresponding results for compounds with 20 and 60 phr of CB filler, respectively. Fig. 4 shows the accumulation of residual strain with the number of loading–unloading cycles for the three compounds. The following observations are made:

- There are large differences in the stresses corresponding to the same strain level under loading and unloading during the first cycle in periodic tests with a fixed strain amplitude. The differences increase with the amount of CB in the compound.

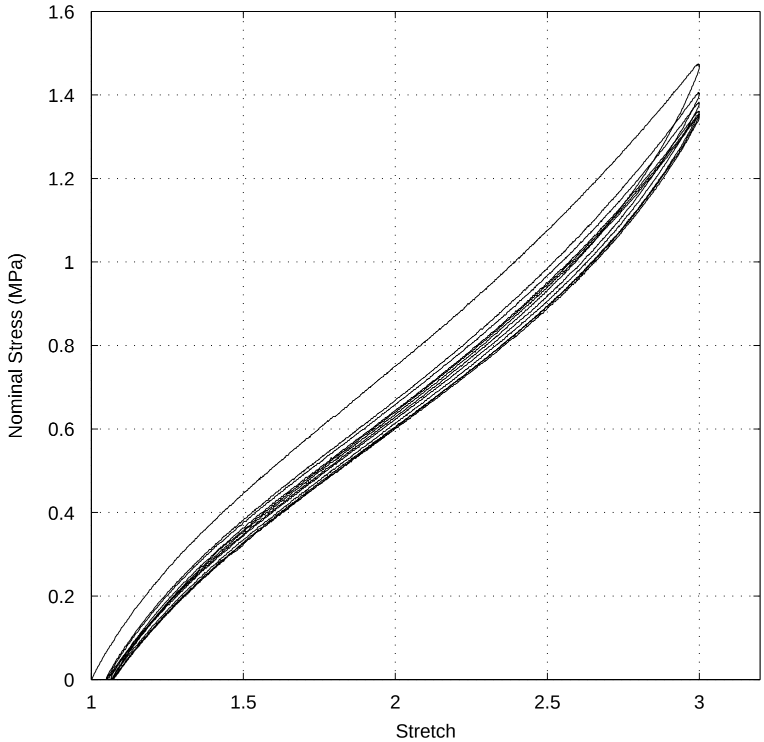

Fig. 1. Pre-conditioning of a particle-reinforced dumbbell specimen with 1 phr of carbon black with maximum stretch $\lambda = 3$.

- There is a reduction in the stress at a given strain on each successive loading. The reduction is largest on the first and second loading–unloading cycles and becomes rather small after about six cycles. Again, the reduction in the stress increases with the amount of CB.
- Residual strains are evident in all three compounds. The major part of the residual strain in each case is generated during the first loading–unloading cycle. The increase in this permanent set continues through all six cycles, but it appears to reach a fixed value, which is largest for the compound with the largest content of CB filler.
- After the six pre-conditioning loading–unloading cycles the stress-stretch responses are essentially repeatable and additional stress softening and residual strain generated are negligible.
- The effects of stress softening and residual strain, even though present, are not of major concern for unfilled compounds and elastomers with a very low content of CB.

We note that the degree of stress softening and the magnitudes of the residual strains are dependent on time and temperature. However, in this study we are not concerned with phenomena such as thermal recovery and viscous effects.

In the second series of experiments, three additional specimens of the same rubber compounds were each subjected to periodic loading up to three different, but fixed, stretches. These tests were all carried out at the same strain rate of $0.02\ \mathrm{s}^{-1}$ and at the same constant room temperature of 25 °C. Each of the specimens was subjected to six loading–unloading cycles up to $\lambda = 1.5$. After completion of the sixth unloading cycle, each specimen was then loaded up to a stretch of $\lambda = 2$ and again subjected to six cycles. The stretch was then increased to $\lambda = 2.5$ and six additional loading–unloading cycles were performed. No recovery time was

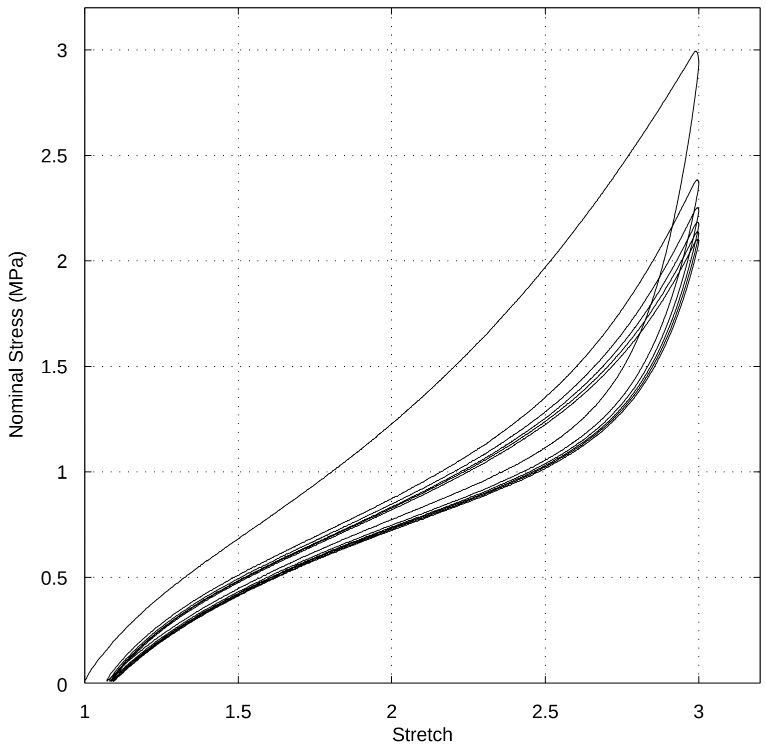

Fig. 2. Pre-conditioning of a particle-reinforced dumbbell specimen with 20 phr of carbon black with maximum stretch $\lambda = 3$.

allowed during the 18 loading–unloading cycles. The results are shown for the compound with 1 phr in Fig. 5 and for the compounds with 20 and 60 phr in Figs. 6 and 7, respectively.

The following additional observations are made.

- The stresses obtained for specimens loaded cyclically up to $\lambda = 1.5$ and successively to $\lambda = 2.0$ and $\lambda = 2.5$ should be compared with those at the same values of stretch for the specimens loaded directly to $\lambda = 3.0$. There is no significant difference for λ up to about 1.5 but thereafter the difference becomes marked with increasing λ.
- The accumulated residual strain depends on the maximum stretch of the specimen during the previous loading cycle, i.e. larger stretch translates into larger residual strain. The residual strain accumulated during the first loading up to a given stretch constitutes the major part; additional cycles up to the same stretch add proportionately less residual strain (see Fig. 8).
- The magnitude of the accumulated residual strain does not depend linearly on the maximum elongation. It can be seen from Fig. 8 that the magnitude of the residual strain is proportionately larger during the initial periodic loading up to $\lambda = 1.5$. Doubling the strain to $\lambda = 2$ does not double the residual strain.
- The degree of stress softening during the first few loading–unloading cycles depends on the maximum elongation achieved. The stress softening is much more severe, for example, for loading to a maximum stretch of $\lambda = 2.5$ than for a maximum stretch of $\lambda = 1.5$.
- All these phenomena depend on the proportion of carbon black in the compound. In particular, both the stress softening and residual strain increase with the filler content.

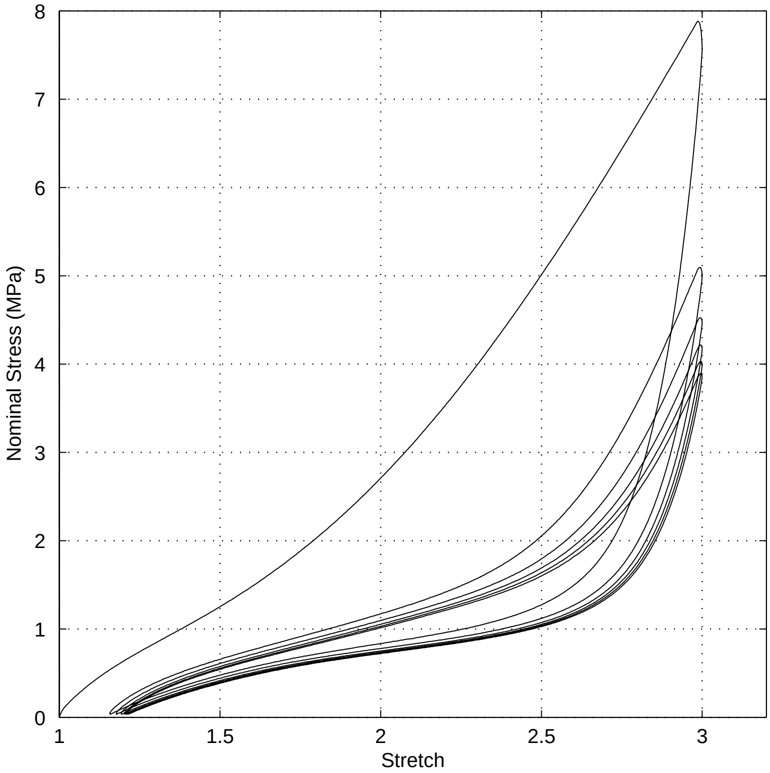

Fig. 3. Pre-conditioning of a particle-reinforced dumbbell specimen with 60 phr of carbon black with maximum stretch $\lambda = 3$.

3. Basic equations

For full details of the relevant theory of elasticity summarized in this section the reader is referred to, for example, Ogden (1984, 2001) and Holzapfel (2000).

We consider a rubberlike solid regarded as a continuous body. Let points of the body be labelled by their position vectors $\mathbf{X}$ in the initial (unstressed) configuration relative to an arbitrarily chosen origin. Suppose that when the body is deformed the point $\mathbf{X}$ has a new position $\mathbf{x}$ in the resulting deformed configuration of the body.

For simplicity we consider only Cartesian coordinate systems and let $\mathbf{X}$ and $\mathbf{x}$ respectively have coordinates X_α and x_i, where $\alpha, i \in \{1, 2, 3\}$, so that x_i depends on X_α.

The deformation gradient tensor, denoted $\mathbf{F}$, is given by

$$\mathbf{F} = \operatorname{Grad} \mathbf{x} \tag{1}$$

and has Cartesian components $F_{i\alpha} = \partial x_i / \partial X_\alpha$, Grad being the gradient operator with respect to $\mathbf{X}$. For a volume preserving (isochoric) deformation we have

$$\det \mathbf{F} = 1. \tag{2}$$

Here, we assume that (2) holds for all deformations, so that the material is *incompressible*.

The deformation gradient can be decomposed according to the (unique) polar decompositions

$$\mathbf{F} = \mathbf{RU} = \mathbf{VR}, \tag{3}$$

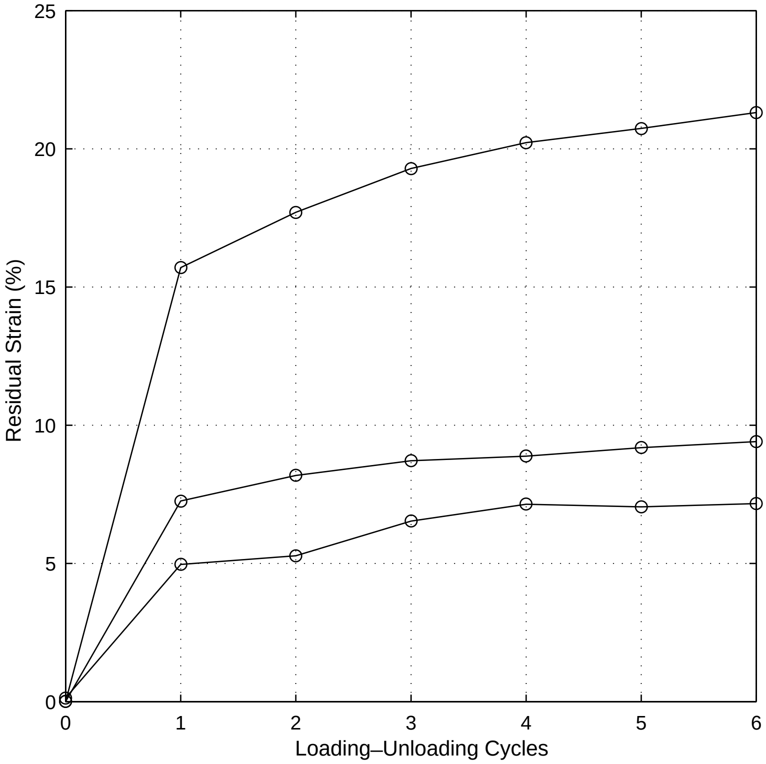

Fig. 4. Accumulation of residual strain for particle-reinforced dumbbell specimen with 1, 20 and 60 phr of carbon black as a function of the number of loading–unloading cycles (constant maximum stretch of $\lambda = 3$).

where $\mathbf{R}$ is a proper orthogonal tensor and the tensors $\mathbf{U}$, $\mathbf{V}$ are positive definite and symmetric, respectively the right and left stretch tensors. These can be expressed in spectral form. For $\mathbf{U}$, for example, we have the spectral decomposition

$$\mathbf{U} = \sum_{i=1}^{3} \lambda_i \mathbf{u}^{(i)} \otimes \mathbf{u}^{(i)}, \tag{4}$$

where the principal stretches $\lambda_i > 0$, $i \in \{1, 2, 3\}$, are the eigenvalues of $\mathbf{U}$, $\mathbf{u}^{(i)}$ are the (unit) eigenvectors of $\mathbf{U}$, referred to as the Lagrangian principal axes, and $\otimes$ denotes the tensor product. It follows from (2)–(4) that

$$\lambda_1 \lambda_2 \lambda_3 = 1. \tag{5}$$

3.1. Hyperelasticity

In the theory of hyperelasticity there exists a strain-energy function, denoted $W = W(\mathbf{F})$, defined on the space of deformation gradients subject, since we are considering incompressible materials, to the constraint (2). The nominal stress tensor, denoted $\mathbf{S}$, is given by

$$\mathbf{S} = \frac{\partial W}{\partial \mathbf{F}} - p\mathbf{F}^{-1}, \quad \det \mathbf{F} = 1, \tag{6}$$

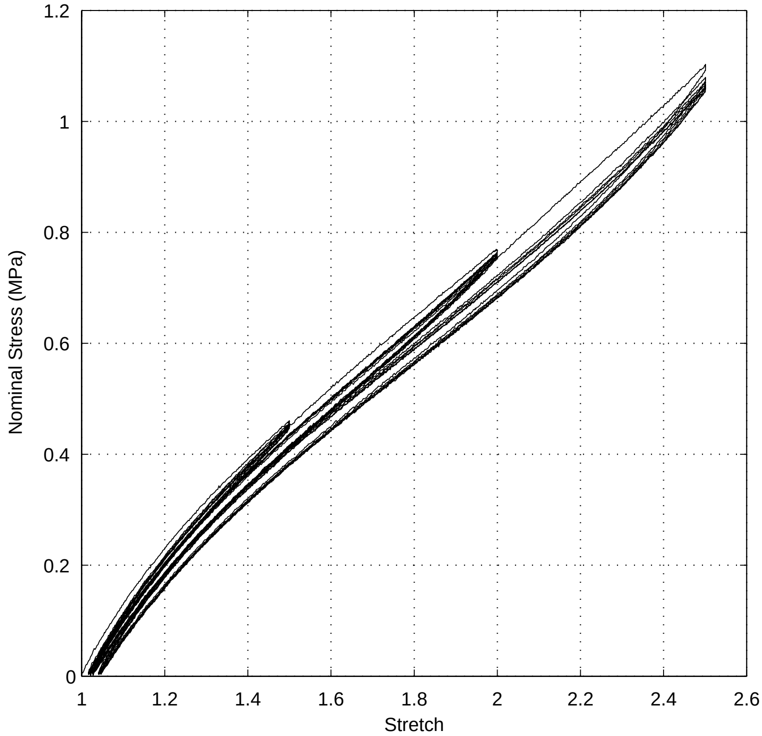

Fig. 5. Periodic uniaxial extension tests of a particle-reinforced dumbbell specimen with 1 phr of carbon black with maximum stretches of $\lambda = 1.5$, $\lambda = 2.0$ and $\lambda = 2.5$.

where p is a Lagrange multiplier associated with the constraint (2) and represents an arbitrary hydrostatic pressure. The Cauchy stress tensor, denoted $\boldsymbol{\sigma}$, is given by

$$\boldsymbol{\sigma} = \mathbf{FS} = \mathbf{F}\frac{\partial W}{\partial \mathbf{F}} - p\mathbf{I}, \quad \det \mathbf{F} = 1, \tag{7}$$

where $\mathbf{I}$ is the identity tensor. We take W and the stress to vanish in the reference configuration.

According to the principle of objectivity, W depends on $\mathbf{F}$ through $\mathbf{U}$ and we write

$$W(\mathbf{F}) = W(\mathbf{U}). \tag{8}$$

The (symmetric) Biot stress tensor $\mathbf{T}$ is then defined by

$$\mathbf{T} = \frac{\partial W}{\partial \mathbf{U}} - p\mathbf{U}^{-1}, \quad \det \mathbf{U} = 1. \tag{9}$$

3.1.1. Isotropic hyperelasticity

For an *isotropic* elastic solid W depends on $\mathbf{U}$ only through the principal stretches $\lambda_1, \lambda_2, \lambda_3$ and is a symmetric function of the stretches. We write this dependence as $W(\lambda_1, \lambda_2, \lambda_3)$. Consequences of isotropy are that $\mathbf{S} = \mathbf{TR}^T$ and that $\mathbf{T}$ is coaxial with $\mathbf{U}$. Thus, similarly to (4), we have

$$\mathbf{T} = \sum_{i=1}^{3} t_i \mathbf{u}^{(i)} \otimes \mathbf{u}^{(i)}, \tag{10}$$

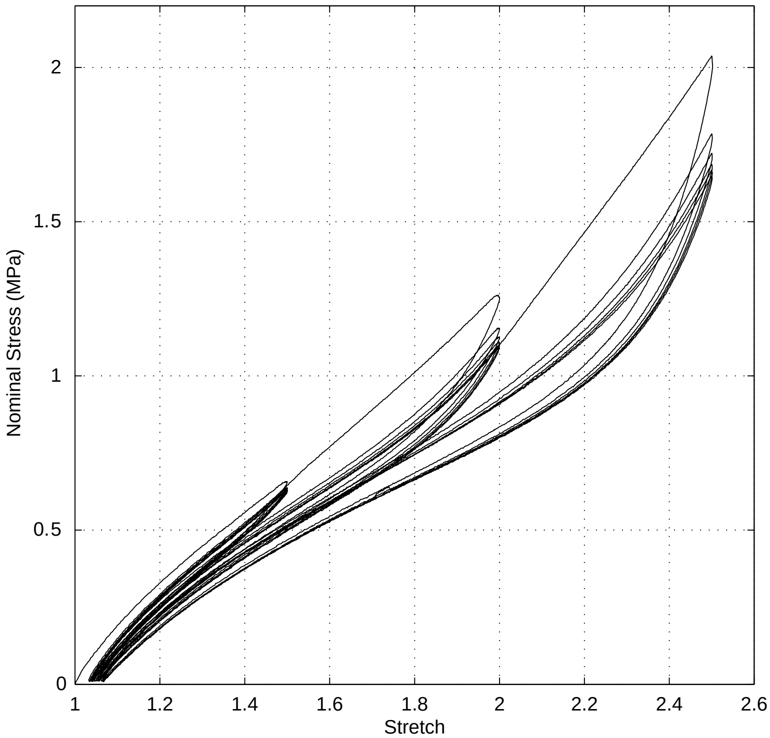

Fig. 6. Periodic uniaxial extension tests of a particle-reinforced dumbbell specimen with 20 phr of carbon black with maximum stretches of $\lambda = 1.5$, $\lambda = 2.0$ and $\lambda = 2.5$.

where t_i, $i \in \{1, 2, 3\}$, are the principal Biot stresses, given by

$$t_i = \frac{\partial W}{\partial \lambda_i} - p\lambda_i^{-1}, \quad \lambda_1\lambda_2\lambda_3 = 1. \tag{11}$$

The principal Cauchy stresses σ_i, $i \in \{1, 2, 3\}$, are

$$\sigma_i = \lambda_i t_i = \lambda_i \frac{\partial W}{\partial \lambda_i} - p. \tag{12}$$

3.1.2. Application to homogeneous biaxial deformations

In this subsection we apply the theory described above to the problem of homogeneous biaxial strain. On use of the incompressibility constraint (5), the strain-energy function can be written in terms of two independent stretches in the form

$$\widehat{W}(\lambda_1, \lambda_2) = W(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}), \tag{13}$$

which is symmetric in λ_1 and λ_2. Then, from (12), after eliminating the pressure p, we obtain the Cauchy stress differences

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial \widehat{W}}{\partial \lambda_1}, \quad \sigma_2 - \sigma_3 = \lambda_1 \frac{\partial \widehat{W}}{\partial \lambda_2}. \tag{14}$$

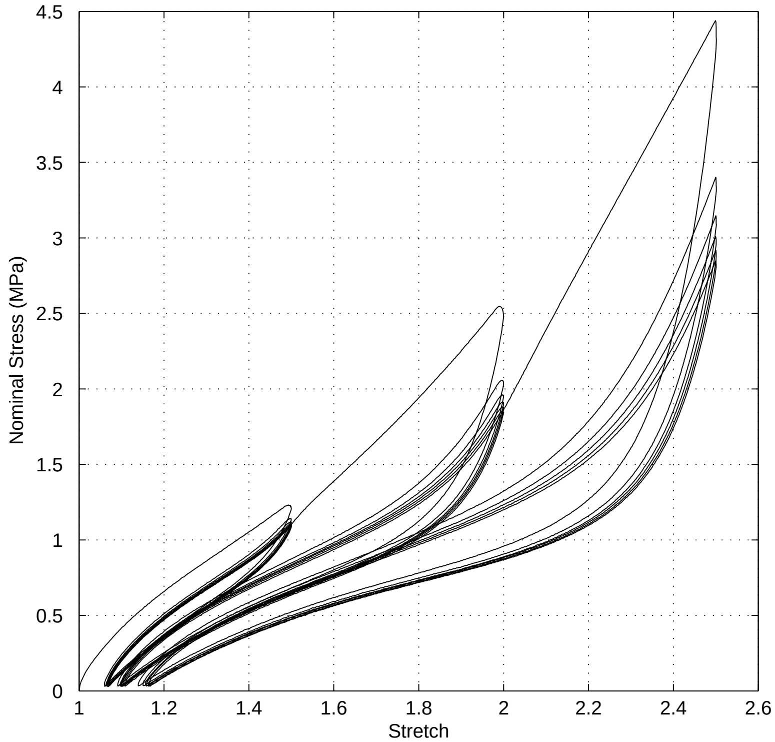

Fig. 7. Periodic uniaxial extension tests of a particle-reinforced dumbbell specimen with 60 phr of carbon black with maximum stretches of $\lambda = 1.5$, $\lambda = 2.0$ and $\lambda = 2.5$.

Eqs. (14) provide a basis for characterizing the form of the energy function using biaxial tests in which λ_1 and λ_2 are varied independently, for more detail we refer to Ogden (1982, 1986, 2003a,b). For this purpose and without loss of generality we can set σ_3 equal to zero so that, in particular, Eq. (14) become

$$\sigma_1 = \lambda_1 t_1 = \lambda_1 \frac{\partial \widehat{W}}{\partial \lambda_1}, \quad \sigma_2 = \lambda_2 t_2 = \lambda_1 \frac{\partial \widehat{W}}{\partial \lambda_2}. \tag{15}$$

Accurate determination of material model parameters included in $\widehat{W}(\lambda_1, \lambda_2)$ requires use of (15) with t_1 and t_2 measured for given pairs of values of λ_1 and λ_2.

3.1.3. Simple tension and compression

In the simple tension (or compression) specialization we take $\lambda_2 = \lambda_3$, and we use the notation

$$\lambda_1 = \lambda, \quad \lambda_2 = \lambda^{-1/2}. \tag{16}$$

The strain energy then depends on the one remaining independent stretch, and we write

$$\widetilde{W}(\lambda) = \widehat{W}(\lambda, \lambda^{-1/2}). \tag{17}$$

In this case $\sigma_2 = \sigma_3 = 0$ and the Cauchy and nominal (or Biot) stresses associated with λ_1 are respectively

$$\sigma = \sigma_1 = \lambda \frac{\mathrm{d}\widetilde{W}(\lambda)}{\mathrm{d}\lambda}, \quad t = \frac{\sigma}{\lambda} = \frac{\mathrm{d}\widetilde{W}(\lambda)}{\mathrm{d}\lambda}. \tag{18}$$

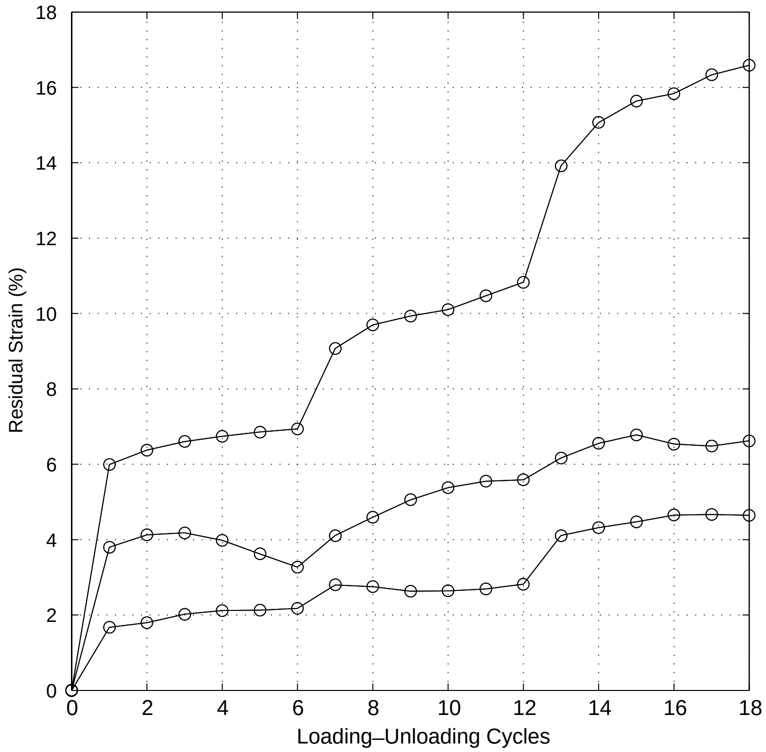

Fig. 8. Accumulation of residual strain for particle-reinforced dumbbell specimen with 1, 20 and 60 phr of carbon black. Periodic loading–unloading is performed with three different, but constant values of maximum stretches, i.e. $\lambda = 1.5$, $\lambda = 2.0$ and $\lambda = 2.5$.

4. Pseudo-elasticity

Based on the theory of pseudo-elasticity developed by Ogden and Roxburgh (1999a,b), we use a strain-energy function $W(\mathbf{F})$ appropriate for hyperelastic materials and modify it by incorporating into it two additional variables, denoted η_1 and η_2. Thus, we write

$$W = W(\mathbf{F}, \eta_1, \eta_2). \tag{19}$$

In the context of the Mullins effect, which is related to material damage, η_1 is referred to as a *damage* or *softening variable*. The Mullins effect was modelled using one such variable by Ogden and Roxburgh (1999a). The second variable η_2 is used here to describe the accumulation of the residual strain in loading–unloading cycles and is referred to as a *residual strain variable*. Both variables depend on the maximum strain achieved previously. The inclusion of η_1 and η_2 provides a means of changing the form of the energy function during the deformation process and hence changing the character of the material properties. In general, the overall response of the material is then no longer elastic and $W(\mathbf{F}, \eta_1, \eta_2)$ is referred to as a *pseudo-energy function*. The resulting theory is referred to as *pseudo-elasticity theory*. In this section we summarize the main ingredients of the theory.

The variables η_1 and η_2 may be active or inactive and a change from active to inactive (or conversely) changes the material properties. This change may, for example, be induced when unloading is initiated.

During primary loading η_1 and η_2 are inactive and we set them equal to a constant value. Without loss of generality, we assume the constant value to be unity and write

$$W_0(\mathbf{F}) = W(\mathbf{F}, 1, 1) \tag{20}$$

for the resulting strain-energy function. The subscript 0 in (20) indicates that the strain-energy function $W_0(\mathbf{F})$ describes the material response when η_1 and η_2 are inactive. For an incompressible material the associated nominal stress is given by

$$\mathbf{S}_0 = \frac{\partial W_0}{\partial \mathbf{F}}(\mathbf{F}) - p_0\mathbf{F}^{-1}, \quad \det \mathbf{F} = 1, \tag{21}$$

where the subscript 0 here and subsequently is used to indicate that η_1 and η_2 are inactive. If η_1 and η_2 become active we take them to depend on $\mathbf{F}$. The nominal stress for an incompressible material subjected to the constraint $\det \mathbf{F} = 1$ is then given by

$$\mathbf{S} = \frac{\partial W}{\partial \mathbf{F}}(\mathbf{F}, \eta_1, \eta_2) + \frac{\partial W}{\partial \eta_1}(\mathbf{F}, \eta_1, \eta_2)\frac{\partial \eta_1}{\partial \mathbf{F}}(\mathbf{F}) + \frac{\partial W}{\partial \eta_2}(\mathbf{F}, \eta_1, \eta_2)\frac{\partial \eta_2}{\partial \mathbf{F}}(\mathbf{F}) - p\mathbf{F}^{-1}. \tag{22}$$

It is convenient to assume that η_1 and η_2 are given implicitly by

$$\frac{\partial W}{\partial \eta_1}(\mathbf{F}, \eta_1, \eta_2) = 0, \quad \frac{\partial W}{\partial \eta_2}(\mathbf{F}, \eta_1, \eta_2) = 0, \tag{23}$$

so that (22) reduces to

$$\mathbf{S} = \frac{\partial W}{\partial \mathbf{F}}(\mathbf{F}, \eta_1, \eta_2) - p\mathbf{F}^{-1}, \quad \det \mathbf{F} = 1, \tag{24}$$

which applies whether or not η_1 and η_2 are active. When η_1 and η_2 are active, the two equations (23) are used to determine η_1 and η_2 in terms of $\mathbf{F}$.

4.1. Isotropy

For an isotropic material the pseudo-elastic energy function (19) assumes the form

$$W(\lambda_1, \lambda_2, \lambda_3, \eta_1, \eta_2), \tag{25}$$

where $(\lambda_1, \lambda_2, \lambda_3)$ are the principal stretches associated with the deformation from the reference configuration. As in Section 3.1.1, W is a symmetric function of the stretches, which are subject to the incompressibility constraint (5). Eq. (23) specialize to

$$\frac{\partial W}{\partial \eta_1}(\lambda_1, \lambda_2, \lambda_3, \eta_1, \eta_2) = 0, \quad \frac{\partial W}{\partial \eta_2}(\lambda_1, \lambda_2, \lambda_3, \eta_1, \eta_2) = 0, \tag{26}$$

which give η_1 and η_2 implicitly in terms of the stretches.

The principal Cauchy stresses σ_i are given by

$$\sigma_i = \lambda_i \frac{\partial W}{\partial \lambda_i} - p, \quad i \in \{1, 2, 3\}, \tag{27}$$

as in (12), but (27) applies whether or not η_1 and η_2 are active.

Since the material is incompressible it is convenient to adapt the notation used in (13) and define the modified pseudo-energy function $\widehat{W}(\lambda_1, \lambda_2, \eta_1, \eta_2)$ by

$$\widehat{W}(\lambda_1, \lambda_2, \eta_1, \eta_2) \equiv W(\lambda_1, \lambda_2, \lambda_1^{-1}\lambda_2^{-1}, \eta_1, \eta_2). \tag{28}$$

Then, on elimination of p from (27), we obtain the principal stress differences

$$\sigma_1 - \sigma_3 = \lambda_1 \widehat{W}_1, \quad \sigma_2 - \sigma_3 = \lambda_2 \widehat{W}_2, \tag{29}$$

where $\widehat{W}_1$ and $\widehat{W}_2$ denote the partial derivatives of $\widehat{W}$ with respect to λ_1 and λ_2 respectively. Eq. (26) are then modified to

$$\frac{\partial \widehat{W}}{\partial \eta_1}(\lambda_1, \lambda_2, \eta_1, \eta_2) = 0, \quad \frac{\partial \widehat{W}}{\partial \eta_2}(\lambda_1, \lambda_2, \eta_1, \eta_2) = 0, \tag{30}$$

and hence η_1 and η_2 are now given implicitly in terms of λ_1 and λ_2 only.

We define the function $\widehat{W}_0(\lambda_1, \lambda_2)$ via

$$\widehat{W}_0(\lambda_1, \lambda_2) \equiv \widehat{W}(\lambda_1, \lambda_2, 1, 1), \tag{31}$$

which is the isotropic specialization of (20). This is the energy function of an incompressible isotropic elastic material for which η_1 and η_2 are inactive. From (29) the specialization (31) yields the stress differences

$$\sigma_{01} - \sigma_{03} = \lambda_1 \widehat{W}_{01}, \quad \sigma_{02} - \sigma_{03} = \lambda_2 \widehat{W}_{02}, \tag{32}$$

where the subscript zero again refers to a deformation path on which η_1 and η_2 are not active and (30) is not operative. A subscript 1 (respectively 2) following the subscript 0 on $\widehat{W}$ indicates partial differentiation with respect to λ_1 (respectively λ_2).

For compatibility with the classical theory $\widehat{W}_0(\lambda_1, \lambda_2)$ must satisfy

$$\widehat{W}_0(1,1) = 0, \quad \widehat{W}_{0\alpha}(1,1) = 0, \quad \widehat{W}_{012}(1,1) = 2\mu, \quad \widehat{W}_{0\alpha\alpha}(1,1) = 4\mu, \tag{33}$$

where $\mu(>0)$ is the shear modulus of the material in the initial (virgin) reference configuration and the index α takes the value 1 or 2.

When η_1 and η_2 are active we suppose that Eq. (30) can be solved explicitly for η_1 and η_2 and we write the solution as

$$\eta_1 = \eta_{e1}(\lambda_1, \lambda_2) = \eta_{e1}(\lambda_2, \lambda_1), \quad \eta_2 = \eta_{e2}(\lambda_1, \lambda_2) = \eta_{e2}(\lambda_2, \lambda_1). \tag{34}$$

Then, an energy function for active η_1 and η_2, symmetrical in (λ_1, λ_2) and denoted $\hat{w}(\lambda_1, \lambda_2)$, may be defined by

$$\hat{w}(\lambda_1, \lambda_2) \equiv \widehat{W}(\lambda_1, \lambda_2, \eta_{e1}(\lambda_1, \lambda_2), \eta_{e2}(\lambda_1, \lambda_2)). \tag{35}$$

From Eqs. (29), (30) and (35) it follows that

$$\sigma_\alpha - \sigma_3 = \lambda_\alpha \partial \hat{w}/\partial \lambda_\alpha = \lambda_\alpha \partial \widehat{W}/\partial \lambda_\alpha, \quad \alpha = 1, 2. \tag{36}$$

4.1.1. Simple tension

As in Section 3.1.3, for simple tension we take $\sigma_2 = \sigma_3 = 0$ and write $\sigma_1 = \sigma$. We also write $\lambda_1 = \lambda$, so that $\lambda_2 = \lambda_3 = \lambda^{-1/2}$, and define $\widetilde{W}$ by

$$\widetilde{W}(\lambda, \eta_1, \eta_2) \equiv \widehat{W}(\lambda, \lambda^{-1/2}, \eta_1, \eta_2). \tag{37}$$

Eqs. (36) and (30) then specialize to

$$\sigma = \lambda \widetilde{W}_\lambda(\lambda, \eta_1, \eta_2) \equiv \lambda t, \quad \widetilde{W}_{\eta_1}(\lambda, \eta_1, \eta_2) = 0, \quad \widetilde{W}_{\eta_2}(\lambda, \eta_1, \eta_2) = 0, \tag{38}$$

wherein the principal Biot stress $t(=t_1)$ is defined and the subscripts signify partial derivatives.

By defining

$$\widetilde{W}_0(\lambda) = \widetilde{W}(\lambda, 1, 1), \tag{39}$$

we may deduce from (33) the specializations

$$\widetilde{W}_0(1) = \widetilde{W}_0'(1) = 0, \quad \widetilde{W}_0''(1) = 3\mu, \tag{40}$$

where the prime signifies differentiation with respect to λ.

This simple tension specialization will be examined in detail in connection with the description of stress softening and accumulation of residual strain in Section 5.

5. A constitutive model for the Mullins effect with residual strain

The theory discussed in Section 4 is a very general framework and allows considerable flexibility in the choice of specific models. To proceed further it is necessary to make such a choice. In this section therefore we choose a simple formulation for the pseudo-elastic energy in order to model the combination of stress softening and residual strain. The material is again taken to be incompressible and (initially) isotropic and we use a pseudo-energy function to represent loading and unloading in the form

$$\widehat{W}(\lambda_1,\lambda_2,\eta_1,\eta_2) = \eta_1\widehat{W}_0(\lambda_1,\lambda_2) + (1-\eta_2)\widehat{N}(\lambda_1,\lambda_2) + \phi(\eta_1,\eta_2), \tag{41}$$

where the function $\widehat{N}$ is introduced in order to characterize the residual strains and the function ϕ is referred to as a *dissipation function*. The latter must satisfy $\phi(1,1)=0$. If we set $\eta_2\equiv 1$, then (41) reduces to the specific model for the Mullins effect developed by Ogden and Roxburgh (1999a).

For the sake of simplicity, we take $\phi(\eta_1,\eta_2)$ to be decoupled in the form

$$\phi(\eta_1,\eta_2) = \phi_1(\eta_1) + \phi_2(\eta_2), \tag{42}$$

where the functions $\phi_1(\eta_1)$ and $\phi_2(\eta_2)$ satisfy

$$\phi_1(1) = 0, \quad \phi_2(1) = 0. \tag{43}$$

From (32), (36) and (41), the Cauchy stress differences are calculated as

$$\sigma_\alpha - \sigma_3 = \eta_1\lambda_\alpha\widehat{W}_{0\alpha} + (1-\eta_2)\lambda_\alpha\widehat{N}_\alpha, \quad \alpha = 1,2 \tag{44}$$

and Eq. (30) become

$$\phi_1'(\eta_1) = -\widehat{W}_0(\lambda_1,\lambda_2), \quad \phi_2'(\eta_2) = \widehat{N}(\lambda_1,\lambda_2), \tag{45}$$

which, implicitly, define the variables η_1 and η_2 in terms of the stretches.

5.1. Uniaxial loading

We define a loading path in (λ_1,λ_2)-space as a path starting from (1,1) on which $\widehat{W}_0$ is increasing. As mentioned by Ogden and Roxburgh (1999a), for many standard forms of strain-energy function $\widehat{W}_0$ is increasing along any straight line path from (1,1) and contours of constant energy are actually convex in (λ_1,λ_2)-space. On the basis of the equations in Section 4.1.1 the specialization of (41) with (42) for simple tension is

$$\widetilde{W}(\lambda,\eta_1,\eta_2) = \eta_1\widetilde{W}_0(\lambda) + (1-\eta_2)\widetilde{N}(\lambda) + \phi_1(\eta_1) + \phi_2(\eta_2). \tag{46}$$

For uniaxial loading from the natural (stress free) configuration the above equation becomes

$$\widetilde{W}(\lambda,1,1) = \widetilde{W}_0(\lambda), \tag{47}$$

where the softening parameter η_1 and the residual strain parameter η_2 are both inactive and each assumes the value unity, as specified in (39). During primary loading of an initially undamaged material, the functions ϕ_1 and ϕ_2 must satisfy (43). The uniaxial Biot stress for primary loading becomes

$$t_0 = \widetilde{W}'(\lambda,1,1) = \widetilde{W}_0'(\lambda). \tag{48}$$

5.2. Uniaxial unloading

When unloading is initiated from any point on the primary loading path, the variables η_1 and η_2 become active and the form of the energy function changes continuously, as does the stress. Using (38) and (46) the Biot stress t is calculated as

$$t = t_1 + t_2 = \eta_1 \widetilde{W}_0'(\lambda) + (1 - \eta_2)\widetilde{N}'(\lambda) = \eta_1 t_0 + (1 - \eta_2)\widetilde{N}'(\lambda), \tag{49}$$

where the contribution of t_1 is associated primarily with the Mullins effect, while that of t_2 is related to the accumulation of residual strain. In Eq. (49) the Biot stress t_0 on the primary loading path at the same value of λ is given by (48).

5.2.1. The softening effect

For (49) to predict the Mullins effect on unloading, at the start of which η_1 is switched on, it is clear that we must have $\eta_1 \leqslant 1$ on the unloading path, with equality only at the point where unloading begins. We take $\eta_1 > 0$, so that t_1 remains positive on unloading until $\lambda = 1$ is reached, at which point t_1 vanishes.

To obtain an expression for the softening parameter η_1 for simple tension we specialize $(45)_1$ to uniaxial unloading, so that

$$\phi_1'(\eta_1) = -\widetilde{W}_0(\lambda). \tag{50}$$

On differentiation of (50) with respect to λ we obtain

$$\phi_1''(\eta_1)\frac{d\eta_1}{d\lambda} = -\widetilde{W}_0'(\lambda). \tag{51}$$

In view of the stress softening requirement discussed above we associate unloading with decreasing η_1. Since $t_0 \equiv \widetilde{W}_0'(\lambda) > 0$ for $\lambda > 1$ it follows from (51) that

$$\phi_1''(\eta_1) < 0, \tag{52}$$

and, as in Ogden and Roxburgh (1999a) and Dorfmann and Ogden (2003), we assume henceforth that this inequality holds. We deduce that $\phi_1'(\eta_1)$ is a monotonic decreasing function of η_1 and hence that in principle η_1 is uniquely determined from (50) as a function of $\widetilde{W}_0(\lambda)$.

It is important to point out that the value of η_1 derived from (50) depends on the value of the maximum principal stretch λ_m on the loading path, as well as on the specific forms of $\widetilde{W}_0(\lambda)$ and $\phi_1(\eta_1)$ employed. Since $\eta_1 = 1$ at any point on the primary loading path from which unloading is initiated, it follows from Eqs. (46) and (50) that

$$\phi_1'(1) = -\widetilde{W}_0(\lambda_m) \equiv -W_m, \tag{53}$$

wherein the notation W_m is defined. This is the current maximum value of the energy achieved on the primary loading path. In accordance with the properties of $\widetilde{W}_0$, W_m increases along a loading path. In view of (53), the function ϕ_1 depends (implicitly) on the point from where unloading begins through the energy expended on the primary loading path up to that point.

When the material is fully unloaded, with $\lambda = 1$, η_1 attains its minimum value, $\eta_{1\,\mathrm{min}}$ say. This is determined by inserting these values into Eq. (50) to give, using the first Eq. in (40),

$$\phi'(\eta_{1\,\mathrm{min}}) = -\widetilde{W}_0(1) = 0. \tag{54}$$

Since the function ϕ_1 depends on the point where unloading begins then so does $\eta_{1\,\mathrm{min}}$, that is it depends, though W_m, on the value of λ_m. The pseudo-energy function (46) has the residual value

$$\widetilde{W}(1, \eta_{1\,\mathrm{min}}, 1) = \phi_1(\eta_{1\,\mathrm{min}}). \tag{55}$$

Thus, in the absence of the term associated with η_2, the residual (non-recoverable) energy $\phi_1(\eta_{1\,\min})$ may be interpreted as a measure of the energy dissipated in the material during the loading–unloading cycle, as discussed by Ogden and Roxburgh (1999a). This is the situation for the idealized Mullins effect, where there is no residual strain. In simple tension $\phi_1(\eta_{1\,\min})$ is then the area between the primary loading curve and the relevant unloading curve. This interpretation requires a slight modification if there is residual strain (Ogden and Roxburgh, 1999b), and in the present situation the role of η_2 has to be considered and will be discussed in Section 5.2.2.

In order to satisfy the above requirements, we select the function ϕ_1 so that its derivative is given by

$$-\phi_1'(\eta_1) = \mu m \tanh^{-1}[r(\eta_1 - 1)] + W_m, \tag{56}$$

where r and m are dimensionless positive material parameters, μ being the shear modulus appearing in (40). By combining Eqs. (50) and (56) and rearranging we obtain

$$\eta_1 = 1 - \frac{1}{r}\tanh\left[\frac{W_m - \widetilde{W}_0(\lambda)}{\mu m}\right]. \tag{57}$$

The minimum value $\eta_{1\,\min}$ of the variable η_1 is attained for $\lambda = 1$, i.e. in the undeformed configuration, and is given by

$$\eta_{1\,\min} = 1 - \frac{1}{r}\tanh\left[\frac{W_m}{\mu m}\right]. \tag{58}$$

Finally, integration of Eq. (56) gives $\phi_1(\eta_1)$ explicitly in terms of the variable η_1 in the form

$$\phi_1(\eta_1) = -\mu m(\eta_1 - 1)\tanh^{-1}[r(\eta_1 - 1)] - W_m(\eta_1 - 1) - \frac{\mu m}{2r}\log[1 - r^2(\eta_1 - 1)^2]. \tag{59}$$

The contribution of t_1 to Eq. (49) describes the softening response and is expressed in terms of the nominal stress on primary loading by $t_1 = \eta_1 t_0$. The variable η_1 is restricted to be equal to 1 at the point where unloading begins, to decay monotonically and to remain positive during unloading. This condition ensures that t_1 remains positive during unloading; however, it does not permit the prediction of a residual strain. We remark that this latter restriction was removed by Ogden and Roxburgh (1999b) so as to predict residual strain with just a single additional variable. However, the second additional variable η_2 used here allows more flexibility to effectively model the residual strain in combination with softening.

5.2.2. The residual strain effect

The additive contribution t_2 to the Biot stress in (49) modifies the overall response such that for $\lambda = 1$ the stress t becomes negative. This is equivalent to having, at zero stress, a residual strain. During primary loading $\eta_2 = 1$ up to the point where unloading begins, but during unloading η_2 must be a decreasing function. Since $t_1 = 0$ at $\lambda = 1$ we have $t = t_2$ at that point. It is convenient to set $\eta_2 = 0$ at $\lambda = 1$ so that $0 \leqslant \eta_2 \leqslant 1$. We also take η_2 to be a monotonic increasing function of λ.

One possible expression, but by no means the only one, which satisfies the above restriction on the limiting values of η_2 is given by

$$\eta_2 = \tanh\left[\left(\frac{\widetilde{W}_0(\lambda)}{W_m}\right)^{\alpha(W_m)}\right] \Big/ \tanh(1). \tag{60}$$

The exponent $\alpha(W_m) \geqslant 1$ describes how the contribution t_2 participates in the overall stress for a given $\widetilde{N}(\lambda)$ in Eq. (49). This formulation ensures that the residual strain depends on the maximum deformation seen by the material at the end of the primary loading process.

The damage function $\phi_2(\eta_2)$ is given implicitly by Eq. $(45)_2$. After specialization to uniaxial loading we have

$$\phi_2'(\eta_2) = \widetilde{N}(\lambda). \tag{61}$$

Using Eq. (60), Eq. (61) can in principle be integrated to give $\phi_2(\eta_2)$, although it does not give an explicit form such as (59).

5.3. Uniaxial reloading

When the material is reloaded starting from any point on the unloading path, the response is again given by (49). During reloading, the energy stored in the material increases and so do the values of η_1 and η_2, according to Eqs. (57) and (60). At the point where the softening variable η_1 and the residual strain variable η_2 become unity, the material will rejoin the primary loading path and upon further loading additional damage will be generated in the material. This increase in damage is, however, only noticed during the next unloading phase.

5.4. Anisotropy

Thus far we have assumed that the material response is isotropic even after unloading and, in particular, when there is residual strain. However, such an assumption is in general untenable, for two main reasons. Firstly, even if there is no residual strain (the idealized Mullins effect being operative) and the original natural configuration is unchanged, the damage caused, by uniaxial deformation for example, must induce a change in material symmetry relative to that configuration since a preferred direction has been generated. This is the direction of the extension, which is recorded by the material and influences the subsequent response, which in this case will be transversely isotropic. For some discussion of this point and related matters we refer to the recent paper by Horgan et al. (2003).

Secondly, when a residual stress arises the natural configuration changes and the material response relative to a different reference configuration in general has a symmetry different from that relative to the original natural configuration. Again, for uniaxial deformation this will generate transverse isotropy. In general, however, these two aspects of induced anisotropy are distinct.

Within the restricted context of pure homogeneous strain, and, in particular, the uniaxial deformation considered here, such anisotropy can be modelled by a strain energy that is a function of the two stretches λ_1 and λ_2 *without* requiring symmetry in these two variables (see, for example, Ogden, 2001). Thus, in (41) we now consider $\widehat{W}(\lambda_1, \lambda_2, \eta_1, \eta_2)$ to be unsymmetric in λ_1 and λ_2. However, we still take $\widehat{W}_0(\lambda_1, \lambda_2)$ to be symmetric since this represents the response from the initial reference configuration, while the lack of symmetry is attributed to $\widehat{N}(\lambda_1, \lambda_2)$. In view of (45) this implies that there is no loss of symmetry associated with η_1, only with η_2. In a more general model in which η_1 and η_2 are not uncoupled as in (42) generation of anisotropy can also be associated with η_1.

The above discussion is the basis for the specific model introduced in the following section, its application to numerical results and comparison with the experimental data discussed in Section 2.

6. A specific material model

The strain energy for incompressible materials suggested by (41), when specialized to uniaxial loading in (46), has Biot stress given by (49), which, for convenience, we repeat here:

$$t = t_1 + t_2 = \eta_1 \widetilde{W}_0'(\lambda) + (1 - \eta_2)\widetilde{N}'(\lambda). \tag{62}$$

To simulate the material response during primary loading shown in Figs. 1–3 and 5–7 we use the elastic strain energy function due to Ogden (1972, 1984), namely

$$W(\lambda_1, \lambda_2, \lambda_3) = \sum_{m=1}^{M} \mu_m(\lambda_1^{\alpha_m} + \lambda_2^{\alpha_m} + \lambda_3^{\alpha_m} - 3)/\alpha_m, \tag{63}$$

where α_m and μ_m are material constants to be determined by experiment and M is a positive integer. Most commonly M is taken to be 3. The constants must satisfy the requirement

$$\sum_{m=1}^{M} \mu_m \alpha_m = 2\mu, \tag{64}$$

where $\mu(> 0)$ is the shear modulus of the material in the natural configuration (see Eq. (33)). The non-linear iterative method known as the Levenberg-Marquardt algorithm (see, for example, Twizell and Ogden, 1983) is used frequently for calculating the constants μ_m and α_m, $m = 1, 2, 3$.

For the simple tension and compression specialization shown in Eq. (16), the strain-energy function $W(\lambda_1, \lambda_2, \lambda_3)$ becomes

$$\widetilde{W}_0(\lambda) = \sum_{m=1}^{M} \mu_m(\lambda^{\alpha_m} + 2\lambda^{-\alpha_m/2} - 3)/\alpha_m. \tag{65}$$

The subscript 0 has been attached to $\widetilde{W}$ since we now use $\widetilde{W}_0(\lambda)$ to describe the primary loading path in simple tension. It follows that the Biot stress during primary loading is given by

$$t_0 = \sum_{m=1}^{M} \mu_m(\lambda^{\alpha_m - 1} - \lambda^{-\alpha_m/2-1}). \tag{66}$$

The stress softening during unloading is included in Eq. (49) primarily through the expression $t_1 = \eta_1 t_0$, where η_1 is given by (57). We recall that $t_1 = 0$ for $\lambda = 1$.

To obtain a negative stress at zero deformation, which is a necessary pre-requisite for including residual strains in the model, we use the neo-Hookean strain energy formulation for $\widehat{N}$ in (41), modified to reflect anisotropy and to include the dependence on the maximum principal stretch that the material has been subjected to during primary loading. The selection of the neo-Hookean model is purely for illustration and could be replaced by alternative models such as the model due to Varga (1966).

The modified neo-Hookean model suggested in this study may then be written as

$$N(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}[\nu_1(\lambda_1^2 - 1) + \nu_2(\lambda_2^2 - 1) + \nu_3(\lambda_3^2 - 1)], \tag{67}$$

where the material parameter ν_i, $i = 1, 2, 3$, depends on the maximum stretch λ_i provided $\lambda_i > 1$. For uniaxial loading Eq. (67) simplifies to

$$\widetilde{N}(\lambda) = \frac{1}{2}[\nu_1(\lambda^2 - 1) + (\nu_2 + \nu_3)(\lambda^{-1} - 1)]. \tag{68}$$

The associated stress contribution t_2 in Eq. (62) is now given by

$$t_2 = (1 - \eta_2)\widetilde{N}'(\lambda) = (1 - \eta_2)(\nu_1\lambda - \bar{\nu}_2\lambda^{-2}), \tag{69}$$

where $\bar{\nu}_2 = (\nu_2 + \nu_3)/2$ and η_2 is given by Eq. (60).

The final expression for the Biot stress, valid for periodic uniaxial tension tests, becomes

$$t = \eta_1 \sum_{m=1}^{M} \mu_m(\lambda^{\alpha_m - 1} - \lambda^{-\alpha_m/2-1}) + (1 - \eta_2)(\nu_1\lambda - \bar{\nu}_2\lambda^{-2}), \tag{70}$$

with $t = t_0$ on primary loading ($\eta_1 = \eta_2 = 1$) and η_1 and η_2 given by (50) and (60), respectively, on unloading.

When $\lambda = 1$ this reduces to

$$t = v_1 - \bar{v}_2, \tag{71}$$

which must be negative for $\lambda_m > 1$.

We now apply this model to simulate the combination of stress softening and residual strain accumulation in the particle-reinforced rubber with 60 phr of carbon black, which, of the three specimens, displays the largest stress softening and residual strain. The experimental data for this compound for periodic loading in tension are shown in Figs. 3 and 7.

6.1. Numerical results

The primary loading is fully determined by the elastic strain energy in Eq. (63) with material parameters μ_m and α_m, $m = 1, 2, 3$. These values are summarized in Table 1, from which we obtain $\mu = 1.24$ MPa. Fig. 9 shows the corresponding numerical results for loading up to $\lambda = 3$ and compares them with the experimental data taken from Fig. 3. At this point unloading is initiated and the variables η_1 and η_2 are activated. The initial softening response is determined by η_1 given by Eq. (57). The dimensionless parameters r and m are determined to be 1.25 and 0.965, respectively.

For small strains the influence of the residual strain affects the stress response through the variable η_2 and the function $\widetilde{N}$ in Eq. (62). It can easily be verified that η_2, given by (60), is a monotonic function decreasing with λ, equal to 1 at the initiation of unloading and 0 when $\lambda = 1$. The rate at which η_2 decreases with λ depends on the maximum strain energy W_m during loading. In this representative example it is found that a linear dependence on W_m for the exponent α is sufficient and we obtain $\alpha = 0.3 + 0.16 W_m/\mu$. To fully determine the function $\widetilde{N}$ in (68), it is necessary to specify the dependence of v_1 on W_m or equivalently λ_m. To do this, we make use of the Biot stress corresponding to $\lambda = 1$ given by (71). For the test data of the 60 phr compound shown in Figs. 3, we find

$$v_1 = 0.4\mu\left[1 - \frac{1}{3.5}\tanh\left(\frac{\lambda_m - 1}{0.1}\right)\right], \tag{72}$$

and $\bar{v}_2 = 0.4\mu$. In Fig. 9 the data are given by the circles and the numerical calculations based on the model by the continuous curves. It can be seen that the fit of the model to the data is good.

With the material parameters given above the model was applied to periodic loading–unloading with maximum stretches of 1.5, 2.0 and 2.5. The numerical results are shown in Fig. 10. Note that during reloading, the stress path follows the previous unloading path until the maximum energy W_m is again reached and both variables η_1 and η_2 become unity. For further loading the material now follows the primary loading path described by the strain-energy function $\widetilde{W}_0$. Fig. 10 shows that the model reproduces the main characteristics of the material behaviour illustrated in Fig. 7. However, we have not compared the numerical results in Fig. 10 with the corresponding data in Fig. 7 since the results in Fig. 10 have not made

Table 1
Summary of model parameters for primary loading curve of the 60 phr compound

Material model parameter, Ogden $M = 3$					
μ_1	α_1	μ_2	α_2	μ_3	α_3
−1.528380	−1.011467	0.222564	4.2047799	−1.13418E−3	−4.398598

The values of μ_1, μ_2 and μ_3 are given in MPa.

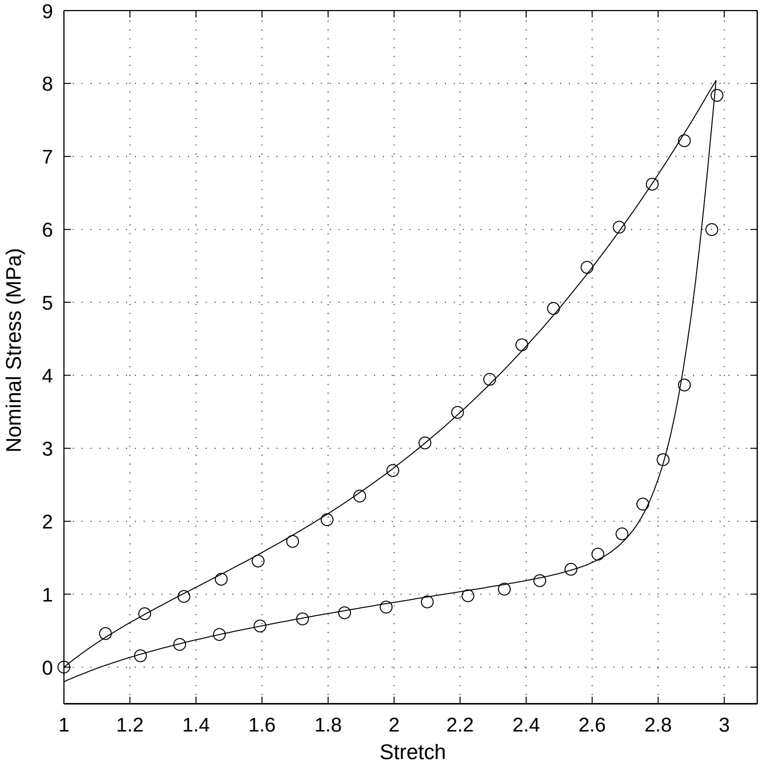

Fig. 9. Comparison of numerical results and experimental data for a particle-reinforced compound with 60 phr of carbon black: nominal stress plotted against stretch.

use of the data for stretches up to $\lambda = 1.5$ and $\lambda = 2.0$. The cyclic loading up to $\lambda = 1.5$ and $\lambda = 2.0$ in effect changes the material properties so that subsequent loading up to a stretch of $\lambda = 2.5$ follows a different path from that experienced if a stretch of $\lambda = 2.5$ is applied directly to the virgin material. This is not accounted for presently in our model.

Let λ_r (which depends on λ_m) be the residual value of λ and let η_{1r} and η_{2r} be the values of η_1 and η_2 for $\lambda = \lambda_r$ given by (50) and (61), respectively. The value of the energy is then $\widetilde{W}(\lambda_r, \eta_{1r}, \eta_{2r})$ and the energy dissipated in the loading–unloading cycle is $W_m - \widetilde{W}(\lambda_r, \eta_{1r}, \eta_{2r})$.

Fig. 11 illustrates the extent of energy dissipation during cyclic loading and unloading as calculated on the basis of Eq. (46). The function ϕ_1 is given by (59) and ϕ_2 can be determined from (61). On each reloading–unloading cycle additional energy is dissipated if the previous value of W_m is exceeded. Fig. 11 shows that the energy returned upon complete unloading is less than the energy expended during loading/reloading.

7. Discussion and conclusions

In this paper the theory of pseudo-elasticity, originally developed by Ogden and Roxburgh (1999a,b) has been used to provide a constitutive model for quasi-static loading–unloading of rubber that accounts for stress softening and residual strain.

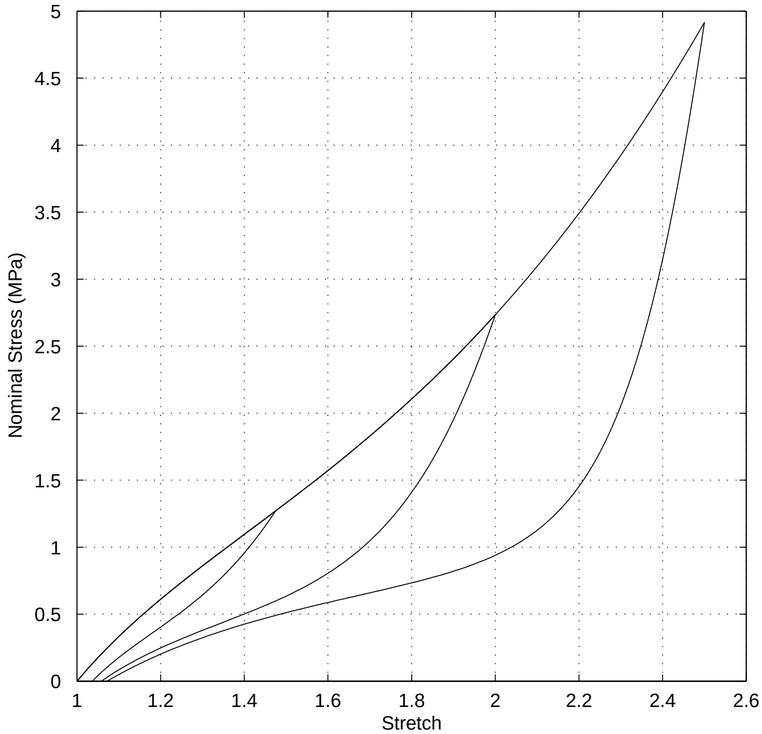

Fig. 10. Comparison of numerical results and experimental data for a particle-reinforced compound with 60 phr of carbon black with maximum stretches $\lambda = 1.5$, $\lambda = 2.0$ and $\lambda = 2.5$: nominal stress plotted against stretch.

The theory uses two deformation-dependent scalar functions to modify the elastic strain-energy function under cyclic loading. A number of material parameters are included in the model to enable the fitting of the simple tension data obtained. The dissipative character of the material is also accounted for.

The suitability of the theory has been demonstrated for a particle-reinforced rubber (filled with 60 phr of carbon black) in the simple case of uniaxial cyclic loading and unloading in tension. It is shown that the model provides a good fit to the experimental data for cyclic loading up to constant value $\lambda = 3$. However, if the same model (with the same material parameters) is used to simulate cyclic loading to smaller fixed stretches, the quality of the fit is less satisfactory. It is important to note that periodic loading–unloading changes the original (virgin) material by introducing a preferred direction, i.e. the material becomes anisotropic. If the material is then subsequently loaded to a higher stretch in the same direction, the response will no longer be the same as the original virgin response. In other words, the idealized Mullins effect, in which the material remains isotropic and residual strain is neglected, does not provide a true representation of the actual material response.

The theory of pseudo-elasticity presented in this paper will therefore be extended to account for the evolving anisotropy and the influence of low strain cycles on higher strain response. The model will include reloading response that differs from the unloading response and hence the hysteresis seen in Figs. 1–3 and 5–7. The theoretical framework described here may also be adapted to more general deformations than the simple tension discussed.

An extension of the theory of pseudo-elasticity to inquire into the thermodynamic and microstructural interpretation supporting the model proposed is under development and will be part of a forthcoming publication.

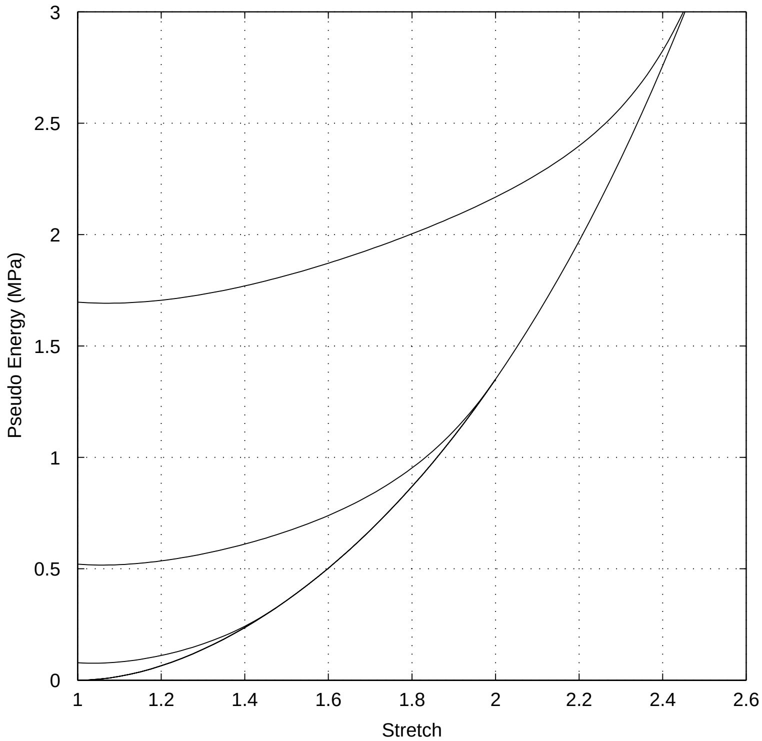

Fig. 11. Plot of the pseudo-energy against the stretch showing the extent of energy dissipation during cyclic loading and unloading.

References

Beatty, M.F., Krishnaswamy, S., 2000. A theory of stress-softening in incompressible isotropic materials. J. Mech. Phys. Solids 48, 1931–1965.

Bergström, J.S., Boyce, M.C., 1998. Constitutive modelling of the large strain time-dependent behavior of elastomers. J. Mech. Phys. Solids 46, 931–954.

Besdo, D., Schuster, R.H., Ihlemann, J., 2001. Constitutive Models for Rubber II. A.A. Balkema, Rotterdam.

Bonart, R., 1968. X-ray investigations concerning the physical structure of cross-linking in segmented urethane elastomers. J. Macromol. Sci. Phys. B 2, 115–138.

Bueche, F., 1960. Molecular basis of the Mullins effect. J. Appl. Polym. Sci. 4, 107–114.

Bueche, F., 1961. Mullins effect and rubber–filler interaction. J. Appl. Polym. Sci. 5, 271–281.

Dannenberg, E.M., 1974. The effect of surface chemical interaction on the properties of filler-reinforced rubber. Rubber Chem. Technol. 48, 410–444.

DeSimone, A., Marigo, J.J., Teresi, L., 2001. A damage mechanics approach to stress softening and its application to rubber. Eur. J. Mech. A—Solids 20, 873–892.

Dorfmann, A., Fuller, K.N.G., Ogden, R.W., 2002. Shear, compressive and dilatational response in rubberlike solids subjected to cavitation damage. Int. J. Solids Struct. 39, 1845–1861.

Dorfmann, A., Muhr, A., 1999. Constitutive Models for Rubber. A.A. Balkema, Rotterdam.

Dorfmann, A., Ogden, R.W., 2003. A pseudo-elastic model for loading, partial unloading and reloading of particle-reinforced rubber. Int. J. Solids Struct. 40, 2699–2714.

Drozdov, A.D., Dorfmann, A., 2001. Stress–strain relations in finite viscoelastoplasticity of rigid-rod networks: applications to the Mullins effect. Continuum Mech. Therm. 13, 183–205.

Ernst, L.J., Septanika, E.G., 1999. A non-Gaussian network alteration model. In: Dorfmann, A., Muhr, A. (Eds.), Proceedings of the First European Conference on Constitutive Models for Rubber, pp. 169–180.

Fung, Y.C., 1980. On the pseudo-elasticity of living tissues. In: Nasser, S.N. (Ed.), Mechanics Today. Pergamon Press, New York, pp. 49–66 (Chapter 4).

Govindjee, S., Simo, J.C., 1991. A micro-mechanically based continuum damage model for carbon black-filled rubbers incorporating the Mullins effect. J. Mech. Phys. Solids 39, 87–112.
Govindjee, S., Simo, J.C., 1992a. Transition from micro-mechanics to computationally efficient phenomenology: carbon black filled rubbers incorporating Mullins' effect. J. Mech. Phys. Solids 40, 213–233.
Govindjee, S., Simo, J.C., 1992b. Mullins' effect and the strain amplitude dependence of the storage modulus. Int. J. Solids Struct. 29, 1737–1751.
Harwood, J.A.C., Mullins, L., Payne, A.R., 1965. Stress softening of natural rubber vulcanizates. 2: Stress softening effects in pure gum and filler loaded rubbers. J. Appl. Polym. Sci. 9, 3010–3021.
Harwood, J.A.C., Payne, A.R., 1966a. Stress softening of natural rubber vulcanizates. 3: Carbon black-filled vulcanizates. J. Appl. Polym. Sci. 10, 315–324.
Harwood, J.A.C., Payne, A.R., 1966b. Stress softening of natural rubber vulcanizates. 4: Un-filled vulcanizates. J. Appl. Polym. Sci. 10, 1203–1211.
Harwood, J.A.C., Payne, A.R., 1967. Stress softening of natural rubber vulcanizates. 5: The anomalous tensile behavior of natural rubber. J. Appl. Polym. Sci. 11, 1825–1834.
Holzapfel, G.A., 2000. Nonlinear Solid Mechanics. Wiley, Chichester.
Horgan, C.O., Ogden, R.W., Saccomandi, G., 2003. A theory of stress softening of elastomers based on finite chain extensibility, Proc. R. Soc. Lond. A, in press.
Johnson, M.A., Beatty, M.F., 1993. A constitutive equation for the Mullins effect in stress controlled uniaxial extension experiments. Continuum Mech. Therm. 5, 301–318.
Johnson, M.A., Beatty, M.F., 1995. The Mullins effect in equibiaxial extension and its influence on inflation of a balloon. Int. J. Eng. Sci. 33, 223–245.
Kaliske, M., Rothert, H., 1998. Constitutive approach to rate-independent properties of filled elastomers. Int. J. Solids Struct. 35, 2057–2071.
Krishnaswamy, S., Beatty, M.F., 2000. The Mullins effect in compressible solids. Int. J. Eng. Sci. 38, 1397–1414.
Lee, M., William, M., 1985. Application of a new structural theory to polymers. 1. Uniaxial stress in crosslinked rubbers. J. Polym. Sci. Polym. Phys. 23, 2243–2271.
Lion, A., 1996. A constitutive model for carbon black filled rubber: experimental investigations and mathematical representation. Continuum Mech. Therm. 8, 153–169.
Lion, A., 1997. On the large deformation behaviour of reinforced rubber at different temperatures. J. Mech. Phys. Solids 45, 1805–1834.
Marckmann, G., Verron, E., Gornet, L., Chagnon, G., Charrier, P., Fort, P., 2002. A theory of network alteration for the Mullins effect. J. Mech. Phys. Solids 50, 2011–2028.
Meisner, B., Matějka, L., 2000. Description of the tensile stress–strain behaviour of filler-reinforced rubber-like networks using a Langevin-theory-based approach. 1. Polymer 41, 7749–7760.
Meisner, B., Matějka, L., 2001. Description of the tensile stress–strain behaviour of filler-reinforced rubber-like networks using a Langevin-theory-based approach. 2. Polymer 42, 1143–1156.
Miehe, C., Keck, J., 2000. Superimposed finite elastic-viscoelastic-plastoelastic stress response with damage in filled rubbery polymers. Experiments, modelling and algorithmic implementation. J. Mech. Phys. Solids 48, 323–365.
Muhr, A.H., Gough, J., Gregory, I.H., 1999. Experimental determination of model for liquid silicone rubber: Hyperelasticity and Mullins effect. In: Dorfmann, A., Muhr, A. (Eds.), Proceedings of the First European Conference on Constitutive Models for Rubber. A.A. Balkema, Rotterdam, pp. 181–187.
Müller, I., 1986. Pseudoelasticity and shape memory. In: Gittus, J., Zarka, J., Nemat-Nasser, S. (Eds.), Large Deformation of Solids: Physical Basis and Mathematical Modelling. Elsevier Applied Science Publishers, Barking, Essex, UK, pp. 107–127.
Mullins, L., 1947. Effect of stretching on the properties of rubber. J. Rubber Res. 16, 275–289.
Mullins, L., 1969. Softening of rubber by deformation. Rubber Chem. Technol. 42, 339–362.
Mullins, L., Tobin, N.R., 1957. Theoretical model for the elastic behaviour of filler-reinforced vulcanized rubbers. Rubber Chem. Technol. 30, 551–571.
Mullins, L., Tobin, N.R., 1965. Stress softening in rubber vulcanizates. Part I. Use of a strain amplification factor to describe the elastic behaviour of filler-reinforced vulcanized rubber. J. Appl. Polym. Sci. 9, 2993–3009.
Ogden, R.W., 1972. Large deformation isotropic elasticity: on the correlation of theory and experiment for incompressible rubberlike solids. Proc. R. Soc. Lond. A 326, 565–584.
Ogden, R.W., 1982. Elastic deformation of rubberlike solids. In: Hopkins, H.G., Sewell, M.J. (Eds.), Mechanics of Solids. Pergamon, New York, pp. 499–537.
Ogden, R.W., 1984. Non-linear Elastic Deformations. Ellis Horwood, Chichester.
Ogden, R.W., 1986. Recent advances in the phenomenological theory of rubber elasticity. Rubber Chem. Technol. 59, 361–383.
Ogden, R.W., 2001. Elements of the theory of finite elasticity. In: Fu, Y.B., Ogden, R.W. (Eds.), Nonlinear Elasticity: Theory and Applications. Cambridge University Press.

Ogden, R.W., 2003a. Nonlinear Elasticity with Application to Material Modelling. Lecture Notes Vol. 6, Centre of Excellence for Advanced Materials and Structures, Polish Academy of Sciences.

Ogden, R.W., 2003b. Elasticity and inelasticity of rubber. In: Saccomandi, G., Ogden, R.W. (Eds.), Mechanics and Thermomechanics of Rubberlike Solids. CISM Courses and Lectures Series 452, Springer, Wien, in press.

Ogden, R.W., Roxburgh, D.G., 1999a. A pseudo-elastic model for the Mullins effect in filled rubber. Proc. R. Soc. Lond. A 455, 2861–2878.

Ogden, R.W., Roxburgh, D.G., 1999b. An energy-based model of the Mullins effect. In: Dorfmann, A., Muhr, A. (Eds.), Proceedings of the First European Conference on Constitutive Models for Rubber, pp. 23–28.

Papoulia, K.D., Kelly, J.M., 1997. Visco-hyperelastic model for filled rubber used in vibation isolation. J. Eng. Mater. Trans. ASME 119, 292–297.

Reese, S., Govindjee, S., 1998. A theory of finite viscoelasticity and numerical aspects. Int. J. Solids Struct. 35, 3455–3482.

Rigbi, Z., 1980. Reinforcement of rubber by carbon black. J. Appl. Polym. Sci. 36, 21–68.

Roland, C.M., 1989a. Network recovery from uniaxial extension. 1. Elastic equilibrium. Rubber Chem. Technol. 62, 863–879.

Roland, C.M., 1989b. The origin of the Mullins effect. Rubber Chem. Technol. 62, 880–895.

Roland, C.M., 1989c. The Mullins effect in crosslinked rubber. J. Rheol. 33, 659–670.

Sedlan, K., 2000. Viskoelastic Materialverhalten von Elastomerwerkstoffen: Experimentelle Untersuchung und Modellbildung. Ph.D. Dissertation, University of Kassel.

Septanika, E.G., Ernst, L.J., 1998. Application of the network alteration theory for modelling the time-dependent constitutive behaviour of rubbers. 2. Further evaluation of the general theory and experimental verification. Mech. Mater. 30, 265–273.

Twizell, E.H., Ogden, R.W., 1983. Non-linear optimization of the material constants in Ogden's stress-deformation relation for incompressible isotropic elastic materials. J. Austral. Math. Soc. B 24, 424–434.

Varga, O.H., 1966. Stress–Strain Behavior of Elastic Materials. John Wiley & Sons, Inc, New York.