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Constitutive modeling of strain-induced softening in swollen elastomers

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ABSTRACT

Under cyclic loading, elastomeric material exhibits strong inelastic responses such as stress-softening due to Mullins effect, hysteresis and permanent set. The corresponding inelastic responses are observed in both dry and swollen rubbers. Moreover, it is observed that inelastic responses depend strongly on the swelling level. For engineering applications involving the interaction and contact between rubber components and solvent, the understanding and consideration of swelling are essential pre-requisites for durability analysis. In this paper, a simple phenomenological model describing Mullins effect in swollen rubbers under cyclic loading is proposed. More precisely, the proposed model adopts the concept of evolution of soft domain microstructure with deformation originally proposed by Mullins and Tobin. The swollen rubbers are obtained by immersing dry ones in solvent until desired degrees of swelling are achieved. Subsequently, their mechanical responses, in particular Mullins effect, under cyclic loading are investigated. These experimental data are used to assess the efficiency of the proposed model. Results show that the model agrees qualitatively well with experiments. Furthermore, the model captures well the fundamental features of strain-induced softening.

1. Introduction

Many engineering applications involve the exposure of elastomeric components to aggressive solvent, e.g. gasket, seal, o-ring or drill packer. In these applications, two material degradations may occur: diffusion of solvent into elastomer leading to swelling and long term cyclic loading leading to fatigue (Ch'ng et al., 2013). Therefore, the understanding and consideration of swelling are essential pre-requisites for durability and performance analysis of such components.

Similarly to dry elastomers, swollen elastomers show significant inelastic responses under cyclic loading: hysteresis, permanent set and stress-softening (Chai et al., 2013a). The hysteresis corresponds to the amount of energy loss during a cycle and can be related to either viscoelasticity (Bergström and Boyce, 1998), viscoplasticity (Lion, 1997) or strain-induced crystallization (Trabelsi et al., 2003). The permanent set refers to the residual extension remaining after a material sample is stretched and released while stress-softening is characterized by the difference between two successive cycles. Stress softening can be defined as a loss of stiffness of the elastomers and consequently affects the elastomers mechanical behavior significantly. The stress-softening in dry rubbers was discovered by Bouasse and Carrière (1903) and was investigated intensively by Mullins (1948). Hence, it is often referred to as the "Mullins effect". Detailed reviews on Mullins effect are provided in Harwood et al. (1967) and more recently in Diani et al. (2009). The general features of Mullins effect can be summarized as below:

1. Stress-softening appears after the first loading at strain level lower than the previously maximum strain attained.
2. When the reloading strain exceeds the previous maximum strain attained, the stress–strain response approach (in many cases follow completely) the reference monotonic uniaxial strain loading.
3. Stress-softening effect increases with the increase in maximum strain.

The early theory which described the softening phenomenon was based on the concept of Mullins and coworkers (Mullins and Tobin, 1957, 1965; Harwood et al., 1966; Harwood and Payne, 1966a,b) who considered that the material consists of two different phases: hard and soft phases. During deformation, an irreversible transformation of hard phase into soft phase takes place. Consequently, the volume fraction of the soft phase increases with deformation resulting to the softening of the equilibrium stress–strain behavior. This concept of hard to soft phase reorganization with

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strain has been used in more recent studies (Qi and Boyce, 2004; Beatty and Krishnaswamy, 2000; Johnson and Beatty, 1993). Other approaches are followed to describe the Mullins effect. Simo (1987) adopted the concept of Continuum Damage Mechanics (CDM). In this case, the Mullins effect is considered as an irreversible damage phenomenon and is described by a scalar damage parameter. Thus, the material response is characterized by multiplying the classical hyperelastic strain energy with a reducing parameter representing damage level. Different forms of damage parameter were proposed in the literature (Chagnon et al., 2004; Ogden and Roxburgh, 1999; Miehe, 1995). Regardless the approach used, it is to note that the above works focused on the Mullins effect in dry rubber. Only few studies dealing with the observation and modeling of Mullins effect in swollen rubbers or gels (Chai et al., 2013b,a; Andriyana et al., 2012; Chai et al., 2011; Lin et al., 2010; Webber et al., 2007).

In the present work, a simple phenomenological model capturing the Mullins effect in swollen rubbers under cyclic loading is proposed. Other inelastic responses such as hysteresis and permanent set are not considered. To this end, the concept of hard-to-soft phase transition initially proposed by Mullins and Tobin (1957) is adopted. Moreover, the approach of Qi and Boyce (2004) for Mullins effect is considered and extended in order to account for swelling.

The paper is organized as follow. In Section 2, experimental program and results probing the Mullins effect in swollen rubber are described. The general framework of the proposed model is presented in Section 3. The efficiency of the model in capturing the effect of swelling on the softening due to Mullins effect is discussed in Section 4. Finally, concluding remarks are given in Section 5.

2. Experimental program

2.1. Materials

Specially designed diabolo rubber specimens are used in the present work. The dimension details are given in our previous study (Ch'ng et al., 2013). It is to note that the middle part of the specimen has an outer diameter of 25 mm and 6 mm thickness. The specimens were obtained by molding a commercial grade of natural rubber with 25 wt% of carbon black and other ingredients to get 60 shore hardness. Due to confidentiality constraint, detailed recipes of the elastomer are not provided here. The swollen elastomeric specimens were obtained by immersing initially dry ones in a standard Malaysia on-road petroleum diesel fuel at room temperature until desired swelling levels were achieved. Note that no standard is followed during the immersion tests. Two swelling levels were considered: 3% and 8% of volume change. For modeling purpose, we introduce the degree of swelling, denoted J_s, defined by:

$$J_s = \frac{V_s}{V_o} \quad (1)$$

where V_s is the specimen volume after immersion (swollen state) and V_o is its initial volume (dry state). J_s for dry, swollen 3% and swollen 8% specimens is equal to 1, 1.03 and 1.08 respectively.

2.2. Mechanical testing

In order to investigate the mechanical characteristics of dry and swollen rubbers, the following mechanical tests were conducted using a conventional Instron testing machine at room temperature:

1. Monotonic uniaxial extension test.
2. Cyclic uniaxial extension test with increasing maximum strain.

In order to avoid excessive increase in the specimen temperature, the tests were performed at a displacement rate of 0.5 mm/s.

2.3. Experimental results

The material responses under monotonic and cyclic loading conditions are presented in Fig. 1. In this figure, stretch is defined by the ratio between the deformed length and the initial one before mechanical test. for swollen rubbers. The lower stress level in swollen rubbers can be attributed to the rubber-solvent interaction which leads to the decrease in the strength of rubber (George et al., 1999).

Both dry and swollen rubbers exhibit strong inelastic responses: stress-softening due to Mullins effect, hysteresis and permanent set. Stress-softening is characterized by the difference in stress levels between two successive uploadings, hysteresis is exhibited by the difference between uploading and unloading paths while permanent set corresponds to the residual strain when the specimen is returned to original position during unloading path. As indicated in Fig. 1, it appears that hysteresis is systematically smaller as the degree of swelling increases. Similar observations have been recently made by Chai et al. (2013a).

Under cyclic loading, in particular during the reloading, it appears that the response of dry rubber does not rejoin the one of monotonic tensile. According to Chagnon et al. (2004), the above observation can be attributed to the viscoelastic characteristics of the material. In the case of swollen rubbers, the viscoelastic effect is reduced by swelling (Chai et al., 2013a). Hence, their reloading responses rejoin the corresponding monotonic tensile responses.

Since Mullins effect is the only inelastic response addressed in the present study, the results of Fig. 1 have to be treated. For this purpose, the data treatment proposed by Chagnon et al. (2004) is adopted and summarized below:

1. Only unloading paths are considered and the reloading paths are assumed to coincide with the downloading paths.
2. The unloading paths are horizontally shifted such that they start from zero strain (stretch = 1).
3. The shifted unloading paths are extended to rejoin the monotonic primary curve.

The resulting treated experimental data are presented in Fig. 2. Using this treated data, following the method detailed in Andriyana et al. (2012), the amount of stress-softening at fourth and eighth unloading curves is calculated and presented in Fig. 3. From this figure, it is observed that the stress-softening decreases as the degree of swelling increases which is consistent with the observation made by Andriyana et al. (2012). In the following, the treated experimental data presented in Fig. 2 will be used to assess the efficiency of the proposed model.

Remark 1. According to Chai et al. (2013b), elastomeric samples swollen up to 3% and 8% are far from thermodynamic equilibrium. Thus, solvent distribution across cross-sections of these specimens is not homogeneous. Being a first attempt to account for the effect of swelling on stress-softening, in the following model development we assume that the material is homogeneous. Consequently, the proposed model provides only a rough estimation of the stress states undergone by the material.

3. Continuum mechanical framework

In this section, the continuum mechanical framework of the proposed model is discussed. The basic concept of hyperelasticity in swollen rubber is recalled. The concept of hard-to-soft phase transition initially proposed by Mullins and Tobin (1957) is

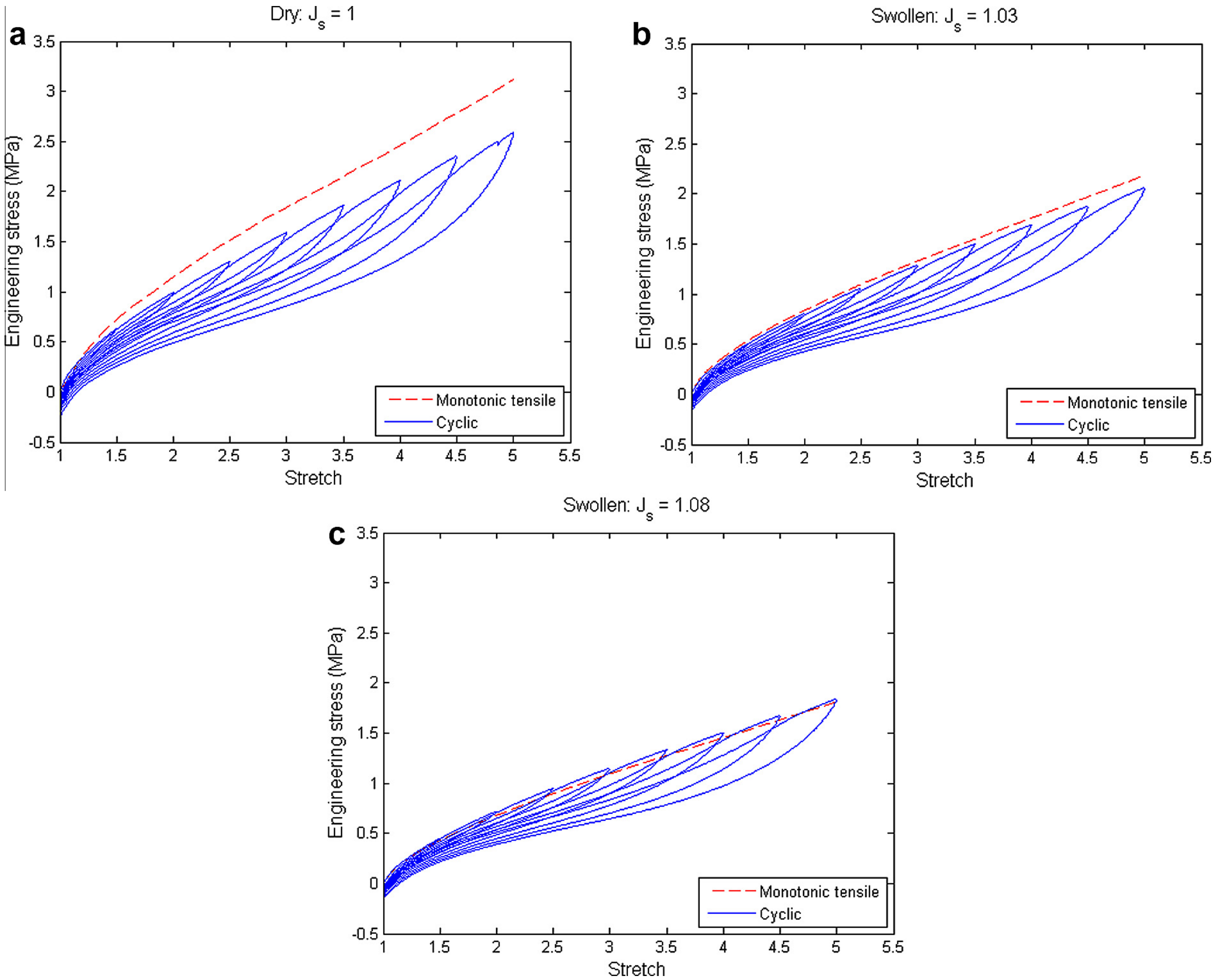

Fig. 1. Monotonic and cyclic tensile experimental results for (a): $J_s = 1$, (b): $J_s = 1.03$ and (c): $J_s = 1.08$. For swollen rubbers, the engineering stress is expressed with respect to swollen-unstrained state.

adopted to describe Mullins effect. Moreover, the approach of Qi and Boyce (2004) for Mullins effect is considered and extended to account for swelling level. Finally, a particularization to the case of uniaxial loading condition is presented.

3.1. Hyperelasticity of swollen rubber

In the following discussion, we postulate swollen rubber as continuous, isotropic and incompressible. Moreover, in order to replicate the experimental procedure whereby the rubber is first subjected to isotropic (stress-free) swelling before undergoing mechanical loading, the total deformation gradient tensor $\mathbf{F}$ is split into two parts:

$$\mathbf{F} = \mathbf{F}_m \mathbf{F}_s = J_s^{1/3} \mathbf{F}_m \quad \text{where } \det \mathbf{F}_m = 1. \tag{2}$$

In the above expression, $\mathbf{F}_s$ and $\mathbf{F}_m$ are the deformation gradient tensors associated with swelling and mechanical loading respectively. In order to describe the stress response, we postulate the existence of a strain energy function W, defined per unit of volume of the material in unswollen–unstrained state which depends on the degree of swelling J_s and on the mechanical part of the deformation gradient tensor $\mathbf{F}_m$ as follow:

$$W = \widetilde{W}(\mathbf{F}) = \widehat{W}(J_s, \mathbf{F}_m) \tag{3}$$

Considering a purely mechanical process, the second law of thermodynamics has the form:

$$\mathcal{D} = \mathbf{P} : \dot{\mathbf{F}} - \dot{W} \geqslant 0 \tag{4}$$

which reduces to:

$$\mathcal{D} = \left(J_s^{1/3} \mathbf{P} - \left.\frac{\partial \widehat{W}}{\partial \mathbf{F}_m}\right|_{J_s} \right) : \dot{\mathbf{F}}_m = 0 \tag{5}$$

for a given (constant) degree of swelling J_s. In this expression, $\mathcal{D}$ is the internal dissipation and $\mathbf{P}$ is the engineering stress tensor with respect to unswollen–unstrained state of the material. Considering objectivity, isotropy and incompressibility, it can be shown that the stress response is given by Holzapfel (2000):

$$\mathbf{P} = q J_s^{-1/3} \mathbf{F}_m^{-T} + 2 J_s^{-1/3} \left[\left(\frac{\partial \widehat{W}}{\partial I_{1m}} + I_{1m} \frac{\partial \widehat{W}}{\partial I_{2m}} \right) \mathbf{F}_m - \frac{\partial \widehat{W}}{\partial I_{2m}} \mathbf{F}_m \mathbf{C}_m \right] \tag{6}$$

where q is an arbitrary scalar (Lagrange multiplier) due to incompressibility assumption which can be determined from the equilibrium equations and appropriate boundary conditions. $\mathbf{C}_m = \mathbf{F}_m^T \mathbf{F}_m$ is the mechanical part of the right Cauchy-Green strain tensor while I_{1m} and I_{2m} are its invariants defined by:

$$I_{1m} = \mathrm{tr}\,\mathbf{C}_m I_{2m} = \frac{1}{2}\left(I_{1m} - \mathrm{tr}\,\mathbf{C}_m^2 \right) \tag{7}$$

The Cauchy stress tensor is simply given by $\sigma = (det\mathbf{F})^{-1}\mathbf{P}\mathbf{F}^{\mathbf{T}}$ which yields to:

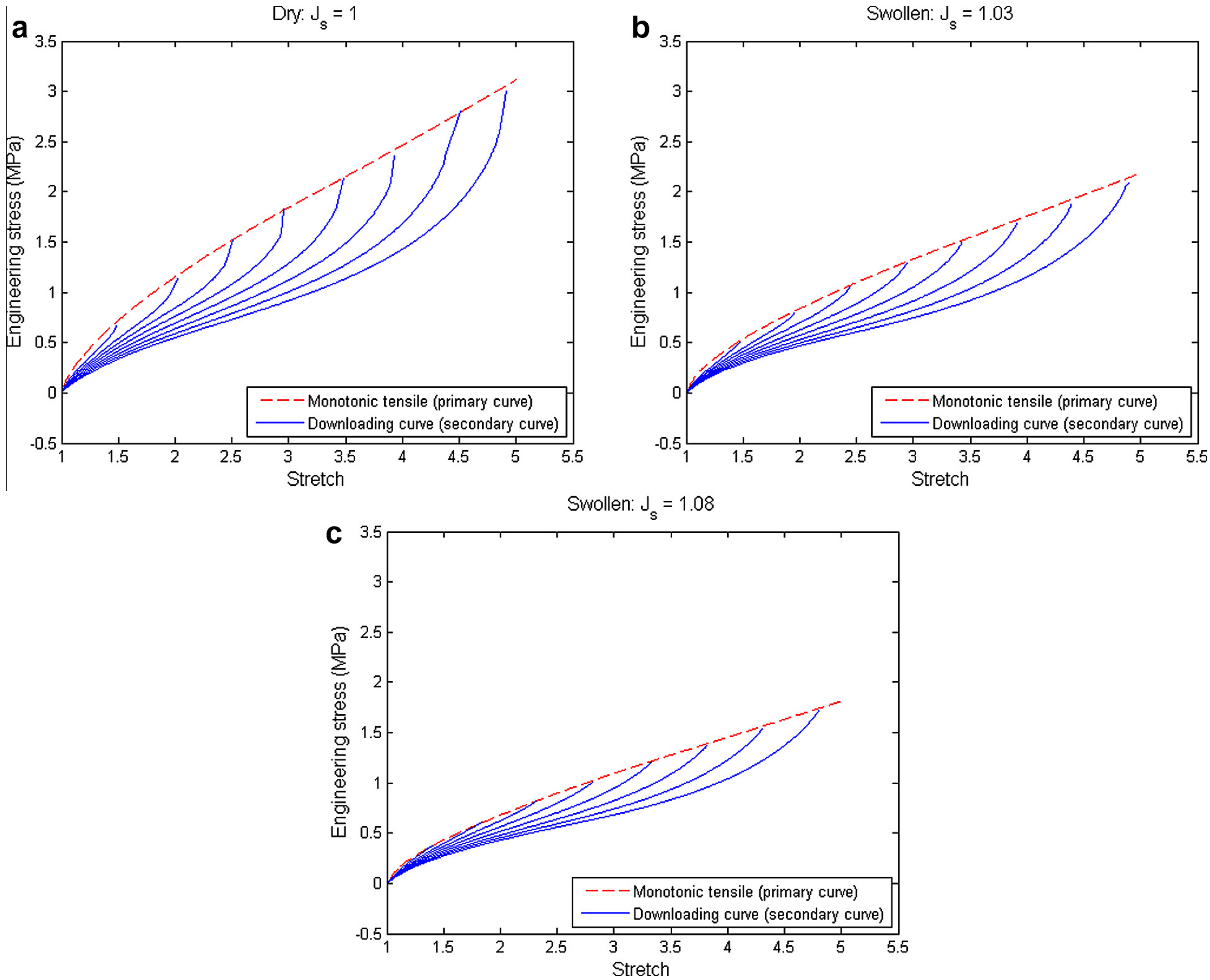

Fig. 2. Treated experimental data for (a): $J_s = 1$, (b): $J_s = 1.03$ and (c): $J_s = 1.08$.

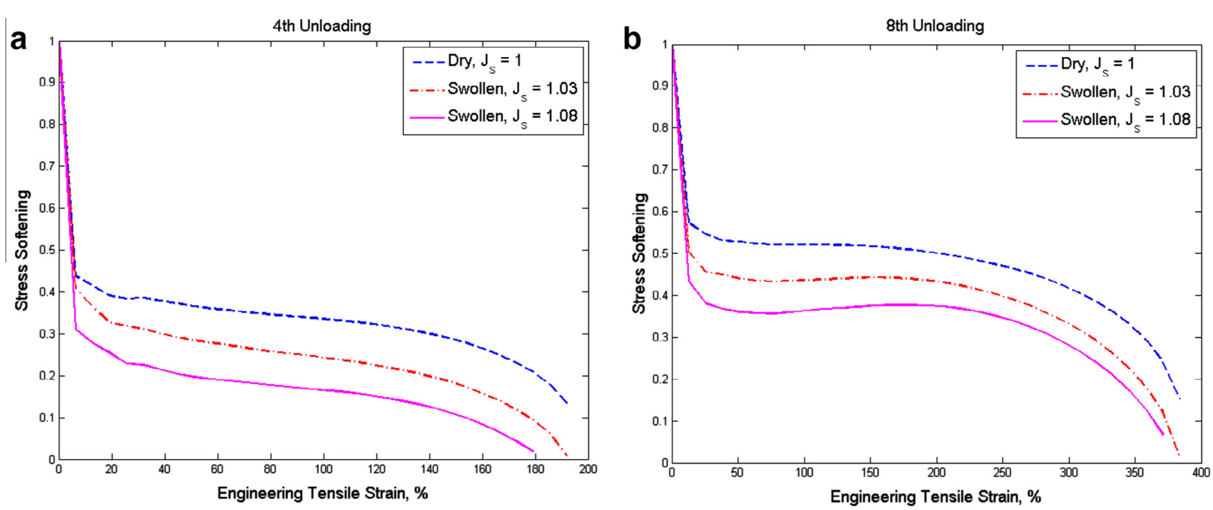

Fig. 3. Stress softening calculated at (a) 4th unloading and (b) 8th unloading.

$$\sigma = qJ_s^{-1}\mathbf{I} + 2J_s^{-1}\left[\left(\frac{\partial \widehat{W}}{\partial I_{1\mathrm{m}}} + I_{1\mathrm{m}}\frac{\partial \widehat{W}}{\partial I_{2\mathrm{m}}}\right)\mathbf{B}_{\mathrm{m}} - \frac{\partial \widehat{W}}{\partial I_{2\mathrm{m}}}\mathbf{B}_{\mathrm{m}}^2\right] \tag{8}$$

In the case when $\widehat{W}$ is chosen to depend on the principal mechanical stretches λ_{im}, the principal Cauchy stresses σ_i can be related to the principal mechanical stretches as follow:

$$\sigma_i = qJ_s^{-1} + J_s^{-1}\lambda_{im}\frac{\partial \widehat{W}}{\partial I_{1\mathrm{m}}} \quad \text{no sum on } i \tag{9}$$

When dealing with swollen rubbers, it is often more convenient to express the engineering stress with respect to swollen-unstrained state of the material, denoted $\widehat{\mathbf{P}}$. Its principal values can be obtained using a simple relation below:

$$\widehat{P}_i = \frac{\sigma_i}{\lambda_{im}} \quad \text{no sum on } i \tag{10}$$

3.2. Extended two-phase model for Mullins effect in swollen rubber

Mullins and Tobin (1957) described filled-rubber as a two-phase system containing a hard phase and a soft phase. The strain is sustained only by the soft phase which percentage increases with the maximum strain applied to the material. The authors suggested that the irreversible conversion from hard phase to soft phase is the origin of the softening observed in rubber under cyclic loading. Since the strain is sustained only by the soft phase, the local strain in the soft phase is necessarily amplified over that of the macroscopic strain. This concept of hard-to-soft phase conversion along with the amplified strain was recently revisited by Qi and Boyce (2004) and will be the basis of our proposed model for the softening in swollen rubber under cyclic loading.

Let υ_s be the effective volume fraction of the soft phase and J_s be the degree of swelling as defined in Eq. (1). For incompressible isotropic swollen rubber undergoing stress-softening due to Mullins effect, the strain energy function (per unit of material volume in unswollen–unstrained state) corresponding to the soft phase has a form:

$$\begin{aligned} W &\equiv \widehat{W}_{\text{sp}}(J_s, \mathbf{F}_{\text{m}}, X(\upsilon_s), \upsilon_s) = \widehat{W}_{\text{sp}}(J_s, \lambda_{1\text{m}}, \lambda_{2\text{m}}, X(\upsilon_s), \upsilon_s) \\ &= W_{\text{sp}}(J_s, \lambda_{1\text{m}}, \lambda_{2\text{m}}, \upsilon_s) \end{aligned} \tag{11}$$

where X is the amplification factor which depends on the soft phase volume fraction υ_s. Following Qi and Boyce (2004), the dependence of X on υ_s is given by:

$$X = 1 + 3.5(1 - \upsilon_s) + 18(1 - \upsilon_s)^2 \tag{12}$$

Considering only mechanical processes and for a given (constant) degree of swelling, the second law of thermodynamics in Eq. (5) becomes:

$$\mathcal{D} = \left(J_s^{1/3}\mathbf{P} - \frac{\partial W_{\text{sp}}}{\partial \mathbf{F}_{\text{m}}}\right) : \dot{\mathbf{F}}_{\text{m}} - \frac{\partial W_{\text{sp}}}{\partial \upsilon_s}\dot{\upsilon}_s \geqslant 0 \tag{13}$$

Using arguments of Coleman and Gurtin (1967), we obtain the following constitutive relations having similar forms to the ones given in Eqs. (9) and (10):

$$\begin{aligned} \sigma_i &= qJ_s^{-1} + J_s^{-1}\lambda_{\text{im}}\frac{\partial W_{\text{sp}}}{\partial \lambda_{\text{im}}} \quad \text{no sum on } i \\ \widehat{P}_i &= \frac{\sigma_i}{\lambda_{\text{im}}} \end{aligned} \tag{14}$$

and the remaining dissipation reduces to:

$$-\frac{\partial W_{\text{sp}}}{\partial \upsilon_s}\dot{\upsilon}_s \geqslant 0. \tag{15}$$

The above inequality must be respected during deformation. The form of W_{sp} and the flow rule $\dot{\upsilon}_s$ describing the increase of soft phase with deformation are specified in the Section 4.1.

Remark 2. The proposed model does not consider general coupling problem between diffusion of solvent and mechanical deformation. Indeed, it focuses on the stress-softening in swollen rubber at a given (constant) degree of swelling J_s. The parameter J_s is introduced merely as a means of defining the state of swelling of the network regardless of whether or not this state is the equilibrium state with respect to the absorption of liquid. Thus, while the proposed model is fitted using experimental data of elastomers swollen at 3% and 8%, it can be used to estimate the stress-softening in elastomers swollen at other (constant) degrees of swelling.

3.3. Special case of uniaxial extension

Without losing generality, we confine the discussion to the case of uniaxial extension along direction $\mathbf{e}_1$. In this case, the tensors $\mathbf{F}_{\text{m}}$ and $\mathbf{B}_{\text{m}}$ are given by:

$$\begin{aligned} \mathbf{F}_{\text{m}} &= \lambda_{\text{m}}\mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{1}{\sqrt{\lambda_{\text{m}}}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3) \\ \mathbf{B}_{\text{m}} &= \lambda_{\text{m}}^2\mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{1}{\lambda_{\text{m}}}(\mathbf{e}_2 \otimes \mathbf{e}_2 + \mathbf{e}_3 \otimes \mathbf{e}_3) \end{aligned} \tag{16}$$

where λ_{m} is the mechanical extension ratio defined by the ratio between the current length of swollen-strained rubber with the one of swollen-unstrained rubber. Using boundary conditions $\sigma_2 = \sigma_3 = 0$ to obtain the Lagrange multiplier q, the non-zero stresses in Eq. (14) are:

$$\begin{aligned} \sigma_1 &= J_s^{-1}\frac{\partial W_{\text{sp}}}{\partial \lambda_{\text{im}}}\left(\lambda_{\text{im}}^2 - \frac{1}{\lambda_{\text{im}}}\right) \\ \widehat{P}_i &= J_s^{-1}\frac{\partial W_{\text{sp}}}{\partial \lambda_{\text{im}}}\left(\lambda_{\text{im}} - \frac{1}{\lambda_{\text{im}}^2}\right) \end{aligned} \tag{17}$$

4. Results and discussion

In this Section, the form of material functions is specified. More precisely, the choice of the strain energy function and the evolution equation for the soft phase consistent with the second law of thermodynamics is described. The strategy to identify material parameters is discussed and the efficiency of the proposed model is assessed using treated experimental data in Fig. 2. Finally, the model behavior under equibiaxial extension and planar extension is simulated.

4.1. Material functions

In order to capture the stress–strain response of rubber at large strain, the eight-chain model of Arruda and Boyce (1993) is retained. The corresponding hyperelastic strain energy density is given by:

$$\begin{aligned} W_{\text{sp}} &= \upsilon_s\mu_d\left[\sqrt{N}\Lambda_{\text{ch,sp}}\beta + N\ln\left(\frac{\beta}{\sinh\beta}\right)\right] \\ \beta &= \mathcal{L}^{-1}\left(\frac{\Lambda_{\text{ch,sp}}}{\sqrt{N}}\right) \end{aligned} \tag{18}$$

where $\mathcal{L}^{-1}$ is the inverse Langevin function, μ_d is the shear modulus of dry rubber, N is the number of chain segments and $\lambda_{\text{ch,sp}}$ is the amplified mechanical chain stretch. The latter is related to the macroscopic mechanical chain stretch λ_{ch} via (Qi and Boyce, 2004):

$$\begin{aligned} \lambda_{\text{ch,sp}} &= \sqrt{X(\lambda_{\text{ch}}^2 - 1) + 1} \\ \lambda_{\text{ch}} &= \sqrt{\frac{I_{1\text{m}}}{3}} \end{aligned} \tag{19}$$

According to Treloar (1975), swelling in rubber is a purely mixing or interdiffusion process with no chemical attraction between rubber and liquid molecules. Furthermore, the only effect of swelling is to reduce the modulus in inverse proportion to the cube root of the swelling degree without changing the form of the stress–strain curves. Following Durning and Morman (1993), the shear modulus of the swollen rubber μ_s is assumed to be related to that of dry rubber μ_d through:

$$\mu_s = J_s^{-n}\mu_d \tag{20}$$

where $n > 0$ is a material parameter. It follows that the strain energy function of rubber (per unit of material volume in unswollen–unstrained state) due to incompressible mechanical loading after isotropically swollen is given by Boyce and Arruda (2001):

$$W_{\rm sp} = v_s\mu_s\left[\sqrt{N}\Lambda_{\rm ch,sp}\beta_{\rm ch,sp} + N\ln\left(\frac{\beta_{\rm ch,sp}}{\sinh\beta_{\rm ch,sp}}\right) - \sqrt{N}J_s^{1/3}\beta_s - N\ln\left(\frac{\beta_s}{\sinh\beta_s}\right)\right] \tag{21}$$

where

$$\Lambda_{\rm ch,sp} = J_s^{1/3}\lambda_{\rm ch,sp}\beta_{\rm ch,sp} = \mathcal{L}^{-1}\left(\frac{\Lambda_{\rm ch,sp}}{\sqrt{N}}\right)$$
$$\beta_s = \mathcal{L}^{-1}\left(\frac{J_s^{1/3}}{\sqrt{N}}\right) \tag{22}$$

Inserting the expression of $W_{\rm sp}$ in Eq. (21) to Eq. (17), the engineering stress relative to swollen-unstrained state is:

$$\widehat{P}_{11} = J_s^{-r}\frac{v_s X\mu_d}{3}\frac{\sqrt{N}}{\lambda_{\rm ch,sp}}\mathcal{L}^{-1}\left(\frac{J_s^{1/3}\lambda_{\rm ch,sp}}{\sqrt{N}}\right)\left(\lambda_{\rm m} - \frac{1}{\lambda_{\rm m}^2}\right)$$
$$r = n + 1/3 \tag{23}$$

It is to note that in the special case of Treloar (Treloar, 1975), i.e. when $n = \frac{1}{3}$, we recover the results of Boyce and Arruda (2001).

The above constitutive equation must be complemented with an evolution equation describing the change in the internal variable v_s consistent with the second law of thermodynamics (Andriyana et al., 2010), more precisely the inequality in Eq. (15). Since $\frac{\partial W_{\rm sp}}{\partial v_s} < 0$, v_s must be an increasing function of maximum deformation state. Adopting a modified form of saturation type of evolution rule as proposed by Qi and Boyce (2004), the evolution of soft phase domain v_s is assumed to follow a non-linear evolution equation below:

$$\dot{v}_s = A(v_{ss} - v_s)\frac{\sqrt{N}-1}{\left(\sqrt{N} - \lambda_{\rm ch,sp}^{\max}\right)^2}\dot{\lambda}_{\rm ch,sp}^{\max} \tag{24a}$$

$$\dot{\lambda}_{\rm ch,sp}^{\max} = \begin{cases} 0 & \text{if} \quad \lambda_{\rm ch,sp} < \lambda_{\rm ch,sp}^{\max} \\ \dot{\lambda}_{\rm ch,sp}^{\max} & \text{if} \quad \lambda_{\rm ch,sp} = \lambda_{\rm ch,sp}^{\max} \end{cases} \tag{24b}$$

In the above expression, $\lambda_{\rm ch,sp}^{\max}$ is the maximum value of amplified mechanical chain stretch $\lambda_{\rm ch,sp}$ during the loading history. A is a material parameter and v_{ss} is the theoretical maximum value of v_s. Integrating Eq. (24), the evolution equation can be recast to:

$$v_s = v_{ss} - (v_{ss} - v_{so})\exp\left[A\left(1 - \frac{\sqrt{N}-1}{\sqrt{N} - \lambda_{\rm ch,sp}^{\max}}\right)\right] \tag{25}$$

where v_{so} is the initial soft phase volume fraction. To summarize, the material parameters that have to be identified from experimental data are given in Table 1.

Table 1
Summary of material parameters required in the proposed model.

Material (soft phase) parameters	μ_d	N	–
Softening parameters	v_{so}	v_{ss}	A
Swelling effect parameter	n	–	–

4.2. Determination of material parameters

In the following, the identification of the material parameters of the proposed model is described. First, it is necessary to determine the parameters corresponding to dry rubber. The properties of the soft domain in dry rubber can be obtained by considering the last unloading curve in Fig. 2(a), i.e. at $\lambda_{\max} = 5$. Since additional softening is expected to occur if the dry rubber was strained beyond $\lambda = 5$, the volume fraction of soft domain at this point is estimated to be $v_s(\lambda_{\max} = 5) \approx 0.90$. Using this value, the parameters μ_d and N are estimated to be $\mu_d = 0.132$ MPa and $N = 28$. Next, by fitting simultaneously the primary curve (monotonic tensile) and unloading curves, the following softening parameters are obtained: $v_{so} = 0.32$, $v_{ss} = 0.92$ and $A = 0.45$.

For swollen rubbers, in order to capture the effect of swelling on the softening (as clearly shown in Figs. 1 and 2), the dependence of parameters v_{so}, v_{ss} and A on the degree of swelling J_s must be examined. For the sake of simplicity, it is assumed here that swelling only affects the initial available soft phase domain v_{so} and parameter A. The parameter v_{ss} being independent of the degree of swelling. More precisely, swelling reduces the initial hard phase domain available to be converted into the soft phase domain

Table 2
Values of material parameters used in the proposed model.

	Parameter	Value
Material (soft phase) parameters	μ_d	0.132 MPa
	N	28
Softening parameters	$v_{so,d}$	0.32
	v_{ss}	0.92
	A_d	0.45
	C_1	0.2
	C_2	0.018
	C_3	0.22
	C_4	0.035
Swelling parameter	n	2.87

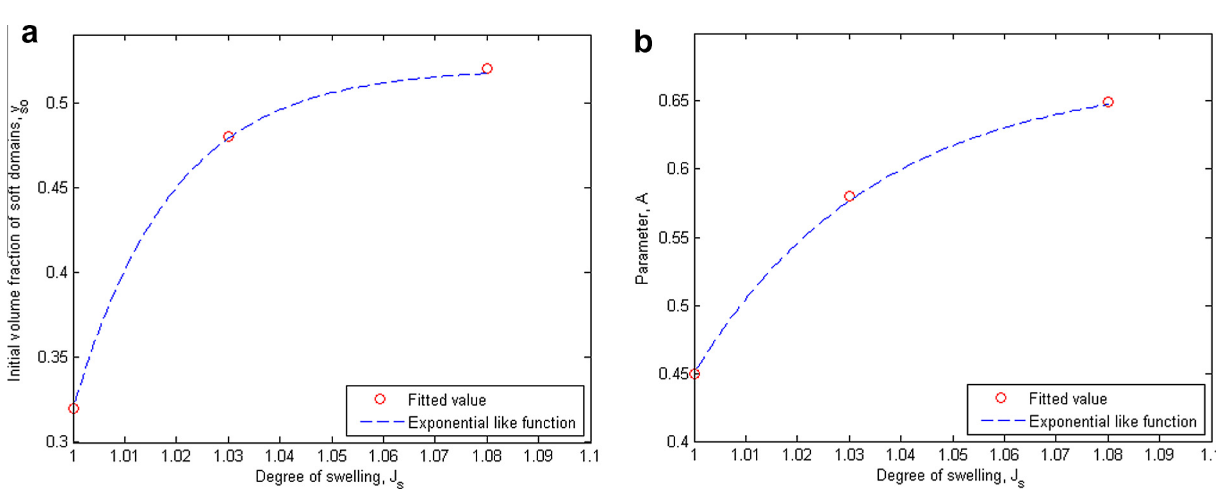

Fig. 4. Evolution of initial volume fraction of soft domain (left) and parameter A as a function of degree of swelling (right).

during deformation process. Indeed, as illustrated in Figs. 1 and 2, stress-softening decreases with the increase in swelling. Consequently, the initial soft phase volume fraction υ_{so} is an increasing function of the degree of swelling. For each degree of swelling, by fitting simultaneously the primary and unloading curves in Fig. 2(a)–(c), we obtain: $\upsilon_{so}(J_s = 1.03) = 0.48$, $\upsilon_{so}(J_s = 1.08) = 0.52$, $A(J_s = 1.03) = 0.58$, $A(J_s = 1.08) = 0.65$ and $n = 2.87$. In Fig. 4, the dependence of υ_{so} and A on J_s is depicted. It appears that the corresponding dependence can be described by the following exponential-like function:

$$\begin{aligned} \upsilon_{so}(J_s) &= \upsilon_{so,d} + C_1\left[1 - \exp\left(-\frac{J_s - 1}{C_2}\right)\right] \\ A(J_s) &= A_d + C_3\left[1 - \exp\left(-\frac{J_s - 1}{C_4}\right)\right] \end{aligned} \tag{26}$$

where $\upsilon_{so,d}$ is the initial volume fraction of the soft phase in dry rubber and A_d is the value of A for dry rubber. $C_1 = 0.21$, $C_2 = 0.018$, $C_3 = 0.22$ and $C_4 = 0.035$ are additional parameters obtained by fitting the points in Fig. 4. Finally, the obtained material parameters are tabulated in Table 2.

Remark 3. The value of $\upsilon_s(\lambda_{\max} = 5)$ is set to 0.9 based on the following considerations:

1. $\lambda_{\max} = 5$ is close to the strain at fracture of $\lambda_f = 6$. Even if υ_s has no direct link to fracture phenomenon, it motivates the consideration that $\upsilon_s(\lambda_{\max} = 5)$ should be close to unity.
2. If $\upsilon_s(\lambda_{\max} = 5)$ is set to another value close to unity such as 0.8 or 0.7, we found that it does not affect significantly the value of other parameters. However, the model fits best with experimental data when $\upsilon_s(\lambda_{\max} = 5)$ is set to be 0.9.

4.3. Comparison to experimental data

The comparisons between the results of the proposed model and treated experimental data are presented in Fig. 5. In general, it is observed that the proposed model shows good agreement with experimental data. The primary curves for dry and swollen rubbers are well-captured. Although there are slight discrepancies during the secondary curve at lower stretch for the dry one but the discrepancies are acceptable and reduce as the stretch increases. As for the swollen rubbers, both primary and secondary curves are well described by the proposed model. Moreover, the dependence of the stress-softening on the swelling level is well-described: smaller softening is observed for higher degree of swelling.

4.4. Simulation for other deformation modes

In order to simulate the response of the model under multiaxial loading conditions, two deformation modes are considered: equibiaxial extension and planar extension. In these two cases, the governing equations needed are summarized below:

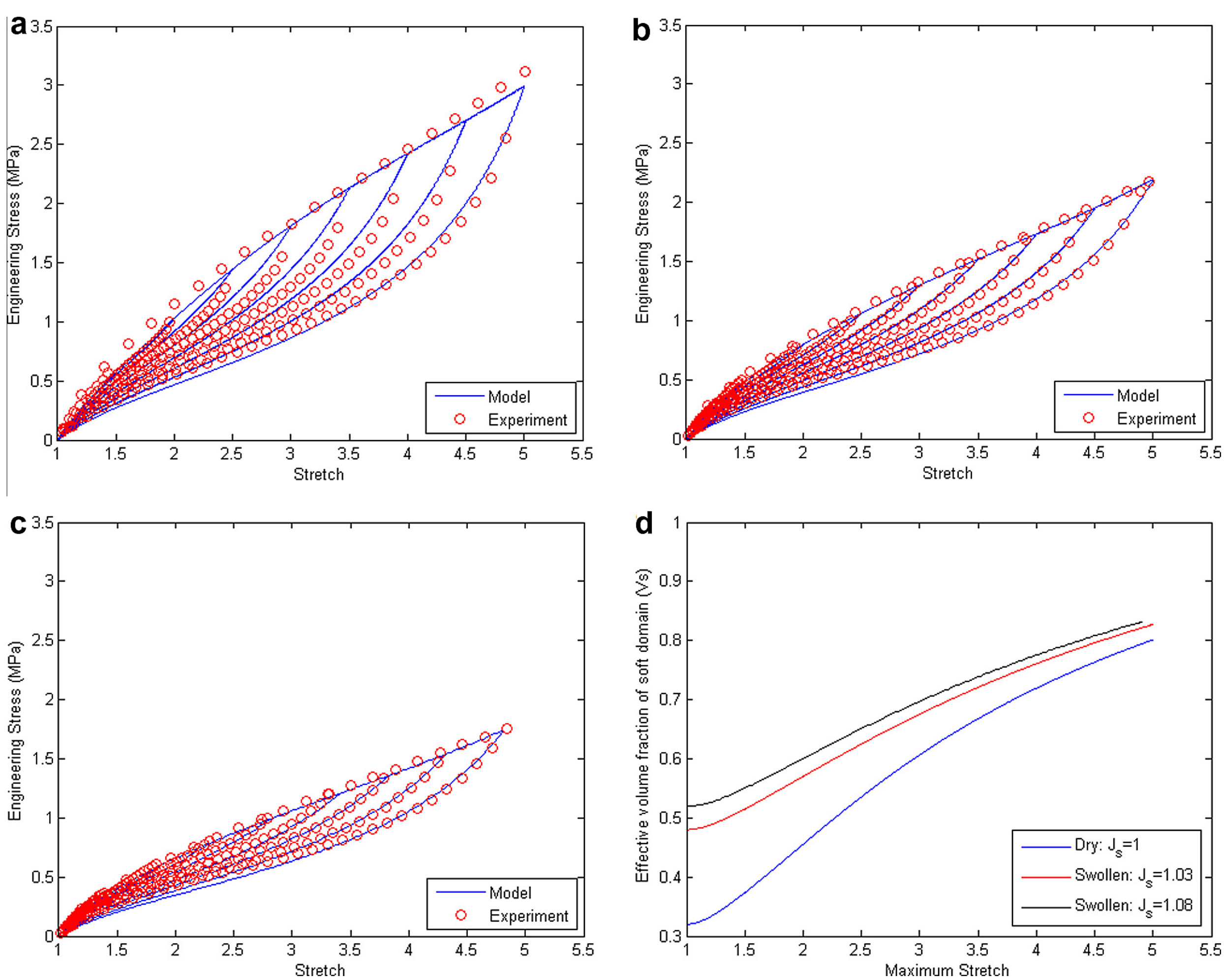

Fig. 5. Comparison between the proposed model and treated experimental data: (a) dry rubber, (b) $J_s = 1.03$, (c) $J_s = 1.08$ and (d) evolution of effective volume fraction of soft phase as a function of maximum mechanical stretch. For swollen rubbers, the engineering stress is expressed with respect to swollen-unstrained state.

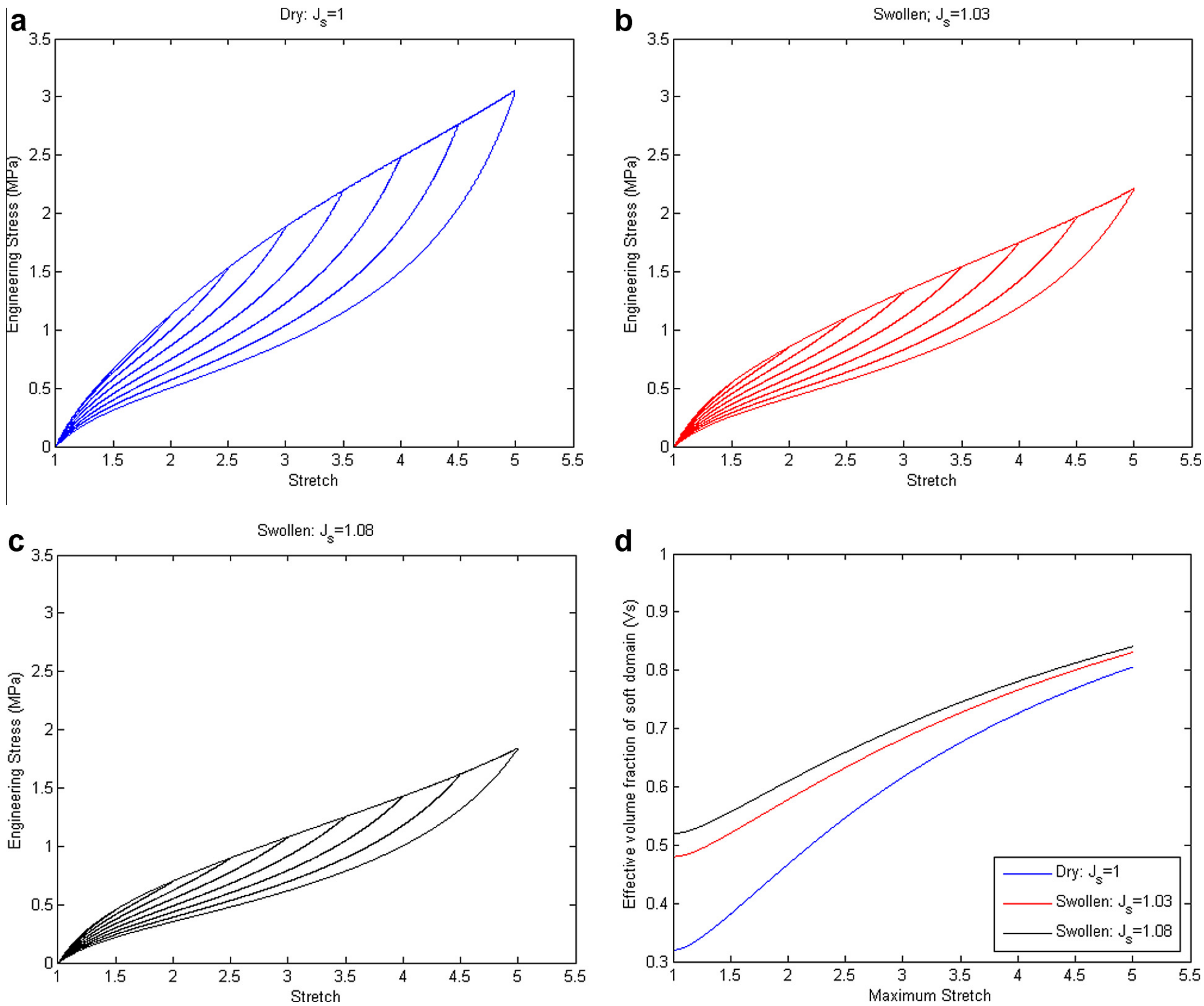

Fig. 6. Model response under planar extension: (a) dry rubber, (b) $J_s = 1.03$, (c) $J_s = 1.08$ and (d) evolution of effective volume fraction of soft phase. For swollen rubbers, the engineering stress is expressed with respect to swollen-unstrained state.

Planar extension

$$\begin{aligned}
\widehat{P}_{11} &= J_s^{-r}\frac{\upsilon_s X\mu_d}{3}\frac{\sqrt{N}}{\lambda_{\mathrm{ch,sp}}}\mathcal{L}^{-1}\left(\frac{J_s^{1/3}\lambda_{\mathrm{ch,sp}}}{\sqrt{N}}\right)\left(\lambda_{\mathrm{m}} - \frac{1}{\lambda_{\mathrm{m}}^3}\right)\\
\lambda_{\mathrm{ch,sp}} &= \sqrt{X(\lambda_{\mathrm{ch}}^2 - 1) + 1}\\
\lambda_{\mathrm{ch}} &= \sqrt{\frac{I_{1\mathrm{m}}}{3}} I_{1\mathrm{m}} = \lambda_{\mathrm{m}}^2 + \frac{1}{\lambda_{\mathrm{m}}^2} + 1
\end{aligned} \tag{27}$$

Equibiaxial extension

$$\begin{aligned}
\widehat{P}_{11} &= J_s^{-r}\frac{\upsilon_s X\mu_d}{3}\frac{\sqrt{N}}{\lambda_{\mathrm{ch,sp}}}\mathcal{L}^{-1}\left(\frac{J_s^{1/3}\lambda_{\mathrm{ch,sp}}}{\sqrt{N}}\right)\left(\lambda_{\mathrm{m}} - \frac{1}{\lambda_{\mathrm{m}}^5}\right)\\
\lambda_{\mathrm{ch,sp}} &= \sqrt{X(\lambda_{\mathrm{ch}}^2 - 1) + 1}\\
\lambda_{\mathrm{ch}} &= \sqrt{\frac{I_{1\mathrm{m}}}{3}}\\
I_{1\mathrm{m}} &= 2\lambda_{\mathrm{m}}^2 + \frac{1}{\lambda_{\mathrm{m}}^4}
\end{aligned} \tag{28}$$

The model behaviors under planar extension and equibiaxial extension are illustrated in Figs. 6 and 7. In each figure, the effect of swelling on macroscopic mechanical response is clearly shown. Indeed, lower stress level is recorded for higher degree of swelling. Moreover, smaller stress-softening is observed when the degree of swelling increases.

The evolution of effective volume fraction of soft phase appears to be dependent on the deformation modes. Indeed, for a given degree of swelling, greatest amount of softening is found in the case of equibiaxial extension than that in planar extension and in uniaxial extension. The corresponding observation can be related to the amount of chain stretch λ_{ch}: for a given strain level, the resulting chain stretch due to equibiaxial extension is the greatest.

5. Conclusions

In this work, a simple model to capture the stress-softening due to Mullins effect in dry and swollen rubbers under cyclic loading has been proposed. For this purpose, the phenomenological approaches of Mullins and Tobin (1957) and Qi and Boyce (2004) for stress-softening were considered and extended in order to account for the effect of swelling. The two models were based on the concept of hard-to-soft phase conversion with deformation along with the local amplified strain.

In order to probe the effect of swelling on stress-softening under cyclic loading, a set of experiments were conducted. It is shown that Mullins effect becomes smaller with the increase of

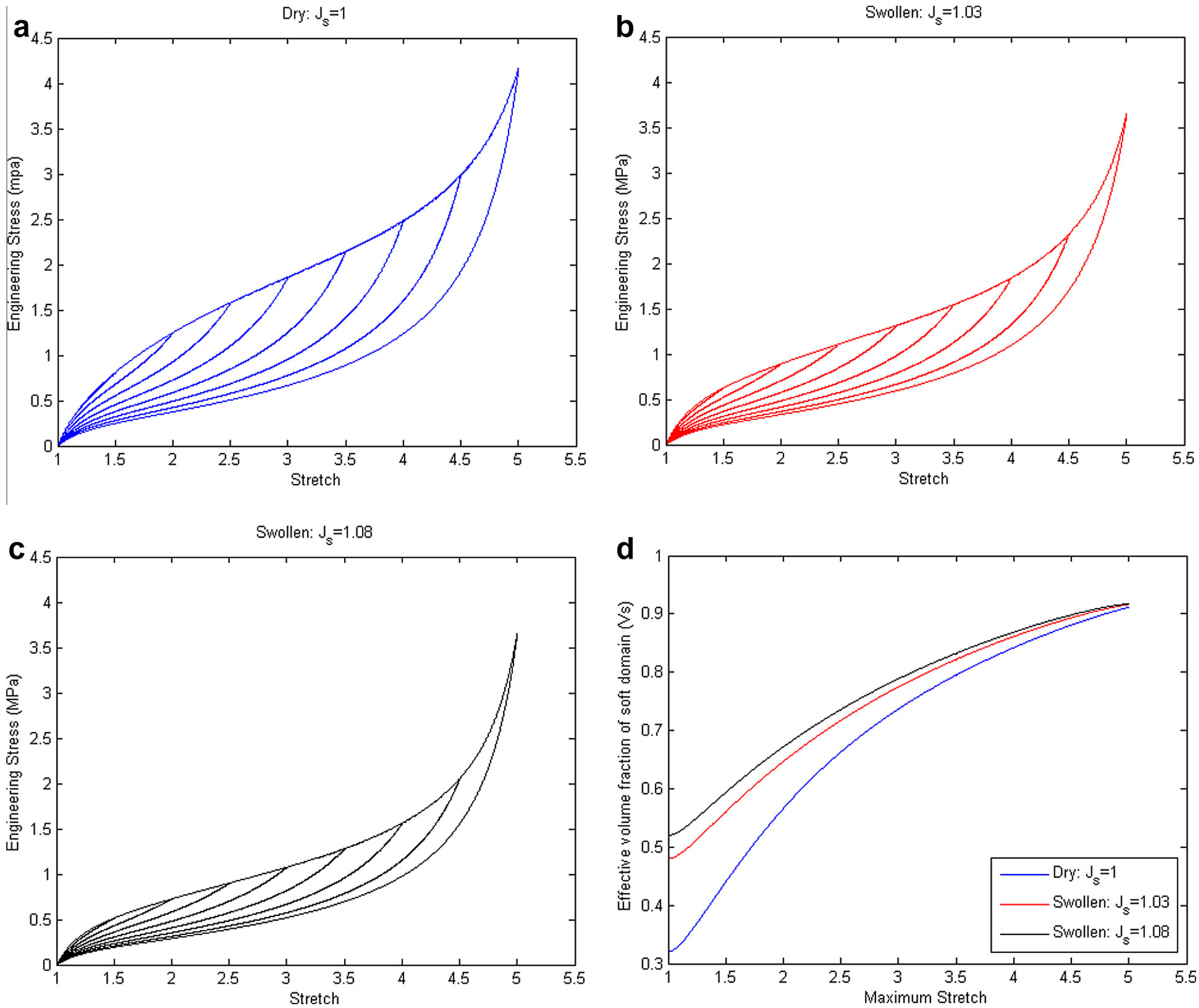

Fig. 7. Model response under equibiaxial extension: (a) dry rubber, (b) $J_s = 1.03$, (c) $J_s = 1.08$ and (d) evolution of effective volume fraction of soft phase. For swollen rubbers, the engineering stress is expressed with respect to swollen-unstrained state.

swelling. Motivated by this observation, it was assumed that the initial available hard phase decreases (initial soft phase increases) with the increase of the degree of swelling. The conversion rate of hard phase into soft phase during deformation is assumed to follow a non-linear saturation evolution rule. The dependence of material shear modulus on swelling was described using the approach of Durning and Morman (1993). The efficiency of the proposed model was assessed. It was found that the proposed model is in good agreement with experimental data.

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