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Constitutive modeling of the Mullins effect and cyclic stress softening in filled elastomers

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The large strain behavior of filled rubbers is characterized by the strong Mullins effect, permanent set, and induced anisotropy. Strain controlled cyclic tests also exhibit a pronounced hysteresis as a strain rate independent phenomenon. Prediction of these inelastic features in elastomers is an important challenge with immense industrial and technological relevance. In the present paper, a micromechanical model is proposed to describe the inelastic features in the behavior of filled elastomers. To this end, the previously developed network decomposition concept [Dargazany and Itskov, Int. J. Solids Struct. 46, 2967 (2009)] is extended and an additional network (CP network) is added to the classical elastic rubber (CC) and polymer-filler (PP) networks. The new network is considered to account for the damage of filler aggregates in the cyclic deformation as the source of hysteresis energy loss. The accuracy of the resulting model is evaluated in comparison to a new set of experimental data.

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I. INTRODUCTION

Rubber-like materials are used in a broad range of industrial products such as tires, seals, and transmission mounts, whose mechanical design requires a deep understanding of physical properties of the material. Generally, mechanical properties of rubber-like materials are strongly improved by addition of fillers (silica or carbon black) due to the creation of new bonds between polymer and filler particles and due to the so-called hydrodynamic effect [1,2]. Usually, fillers in a rubber matrix cannot be found in the form of single particles, but as fractal clusters generally known as aggregates. Aggregates can further join together and form superstructures called agglomerates.

The behavior of filled rubbers under cyclic uniaxial tension is rather complex and characterized by many important inelastic features such as the Mullins effect, permanent set, deformation induced anisotropy, and hysteresis. Despite numerous studies on this subject, the origin of the inelastic behavior in filled elastomers still remains a controversial issue, and modeling all of its features goes beyond the capabilities of the existing micromechanical models. In this work, we propose a new concept of inelasticity in filled elastomers and support it by experimental observations. A micromechanical model developed on the basis of this concept can predict all the aforementioned inelastic effects at the same time without using any phenomenological damage function.

Generally, reloading of filled rubbers leads to smaller stress values in comparison to the ones of initial loading as far as the stretch level does not exceed the maximal stretch of the loading history. This phenomenon was studied in details by Mullins and co-workers [3–7] and is called the Mullins effect. In our own experiments we have observed that at the room temperature the Mullins effect partly recovers after a relatively long resting time (more than a week) and can thus be considered as a quasistatic phenomenon [8].

The stress softening is maximal in the first cycle but reduces in the subsequent cycles until it reaches a constant value hereinafter referred to as hysteresis [see Fig. 1(a)]. In an ideal quasistatic loading, the hysteresis was generally considered to be zero in all deformation cycles except the first one and thus it was neglected [9,10]. The resulting behavior is referred to as the idealized Mullins effect.

Filled rubber samples also show a pronounced residual deformation after the first loading. This residual deformation has long been thought to be a strain rate dependent phenomenon that will disappear if the deformation rate is small enough. Thus, the residual strain has often been eliminated from reported results, by shifting the unloading curve to zero strain in the stress free state [4]. The strong influence of the deformation history on the mechanical behavior in different directions is also reported in numerous publications (see, e.g., [3,8,11]). For example, rubber is isotropic in the virgin state but becomes anisotropic after the first cycle of deformation. This phenomenon is generally referred to as induced anisotropy [see Fig. 1(a)].

The magnitude of the inelastic effects depends on the filler concentration. Unfilled rubbers are considered as elastic materials; however, by addition of fillers, they exhibit several inelastic effects. During the last decades, many phenomenological and micromechanical models have been proposed to predict the inelastic behavior of filled elastomers. In an early approach, Bueche [12,13] associated the Mullins effect with the breakage of weak bonds between polymer chains and filler particles [14]. This assumption was reformulated as the slippage of the polymer chains on the filler clusters [15,16]. Following the lead of Bueche, Govindjee and Simo decomposed the rubber matrix into the pure rubber (CC) and the polymer-filler (PP) network, the latter one being subjected to damage [17,18]. The rubber network was represented by an isotropic three-chain model [19] described by principal stretches. In this model, damage occurs due to the presence of fillers. This assumption was severely criticized [6,7,20] due to its inability to describe stress softening in unfilled rubbers, although recent experiments show that only unfilled elastomers that can crystallize show pronounced stress softening [21]. Within the so-called network alteration concept, the Mullins effect was further described as a result of the breakage of network cross-links [20,22]. The broken chains join together and form fewer, longer chains. The model mainly followed...
the concept of the 8-chain network model [23] based on the non-Gaussian statistical theory proposed by Kuhn and Grün [23]. Zhao further implemented the theory of interpenetrating networks [24] into the network alteration theory to describe the inelastic effects and instability in rubber and double-network hydrogels [25]. Despite comparable mechanical behavior of double network hydrogels and filled rubbers, the sources of their mechanical characteristics are basically different [26]. Experimental observations reveal that hydrogels, unlike rubbers, undergo permanent microstructural damage in the course of deformation, exhibit no recovery after long relaxation times [26], and show almost no hysteresis in second and subsequent load cycles [27]. Cantournet et al. [28] associated the Mullins effect in rubber with the sliding of the macromolecular and connection of chains to the filler particles. The obtained model could predict stress softening without a damage function.

To further include permanent set, Wineman and Rajagopal [29] developed a set of integral type constitutive equations to govern the microstructural damages induced by the rupture of molecular bonds and by the recreation of new ones. Using the concept of flexed and extended polymer chains, Drozdov and Dorfmann [30] developed a micromechanically motivated model that can take stress softening and permanent set into account.

Later Dorfmann and Ogden used the concept of pseudoeffectiveness and proposed a phenomenological approach to also account for the permanent set [31,32]. In order to describe the anisotropic Mullins effect Göktepe and Miehe [33] exploited the idea of the network decomposition by Govindjee and Simo [17]. They generalized the model to three dimensions by means of a microsphere model with 21 material directions. Hanson et al. [34] associated the anisotropic Mullins effect with the removal of chain entanglements during slippage of chains with each another. Thus, despite the constant number of active chains, the density of entanglements changes during deformation. In another approach, Diani et al. [11] further developed the Wang-Guth model and introduced a damage function to govern the energy losses in different spatial directions. The so-obtained model agrees well with the results of quasistatic experiments with respect to the residual strain and induced anisotropy. Merczel et al. [35] proposed a tensor-based constitutive approach for an analytical description of the three-dimensional damage in an arbitrary full network model. We also proposed a micromechanical model for filled rubber-like materials [36], which did not utilize a phenomenological damage function. The model was based on the idea of the network decomposition [17] where the rubber network is subdivided into a pure rubber network CC and a polymer-filler network PP. Damage only takes place in the PP network as a consequence of chain sliding on or debonding from the aggregates. The proposed model demonstrated very good agreement with experimental data and had only a few number of material parameters.

In this work, we present a new micromechanical model to predict all the aforementioned inelastic features in filled rubbers. In contrast to our previous model of network evolution [37,38], the main goal here is to take hysteresis additionally into account. To this end, a new network CP is introduced and added to the former CC and PP networks in the framework of the aforementioned network decomposition concept. The CP network accounts for the deformation and breakage of aggregates which is considered to play a major role in the hysteresis observed in the behavior of filled rubbers.

The paper is organized as follows. In Sec. II, the CP network is introduced and divided into a number of subnetworks composed of microcells. The mechanics of a single microcell is further studied in Sec. III. On this basis, the mechanical response of the subnetwork is described in the case of uniaxial tension in Sec. IV. Then, the micro-macro transition is accomplished in Sec. V and the final response of the CP network in cyclic deformation is thus predicted. Finally, the model is validated by comparing to a new set of experimental data presented in Sec. VI.

II. NETWORK DECOMPOSITION

In the following, we refer to the term “polymer chain” as a part of polymer macromolecules bonded to other parts of the network at its ends. A bond can be considered as a cross-linkage to another polymer chain or a local adsorption on the aggregate surface. Accordingly, one considers different types of polymer chains: with cross-links at both ends (CC), with filler adsorptions at both ends (PP), and with a cross-link at one and a particle adsorption at the other end (CP) (see Fig. 2).

In our previous models, only CC and PP chains were considered in calculation of the energy of the rubber matrix. Aggregates have mostly been considered as rigid bodies. Here, the third network is introduced which consists of aggregates
and CP chains. Within this new network, deformation of aggregates plays an important role. By means of the CP network, we can calculate the deformation of aggregates and localized strains of polymer chains near aggregates. Thus, we can include the energy contributions of aggregates and CP chains to the energy of the rubber matrix.

Although the aggregates are considered within the PP network as well, the contribution of their deformation to the energy of the PP network is not taken into account. The energy of the PP network results from the deformation PP chains due to the relative motion of aggregates. Since the CP and the PP networks are connected via the aggregates, their deformations affect both networks.

Considering contributions of these three networks separately, one can represent the strain energy of the rubber matrix as

$$\Psi = \Psi_{CC} + \Psi_{PP} + \Psi_{CP},$$

where $\Psi_{CC}$, $\Psi_{PP}$, and $\Psi_{CP}$ denote, respectively, the total energies of the CC, PP, and CP network relative to the unit volume of rubber.

**CC network.** The pure rubber network is considered as an ideally elastic network with affine motion of cross-links and identical chains which initially are all in the unperturbed state in which the mean end-to-end distance of a chain is $R_0$. Accordingly, the entropic energy of a single chain with $n$ segments subjected to elongation $\lambda^d$ is represented by $\psi_p(n, \lambda^d R_0)$. Thus, the total strain energy of the CC network that consists of $N_c$ chains with $n_c$ segments in each spatial direction is given by

$$\Psi_{CC} = \frac{1}{A_s} \int_S N_c \psi_p(n_c, \lambda^d R_0) d\mathbf{u},$$

where $A_s$ represents the surface area of the microsphere $S$, and $d\mathbf{u}$ is the unit area of the surface with the normal direction $\mathbf{d}$.

**PP network.** The evolution of the polymer-filler (PP) network is assumed to be responsible for stress softening. Let $N(n, \bar{r})$ be the number of chains with the number of segments (relative length) $n$, the relative end-to-end distance $\bar{r}$, and the end-to-end direction specified by the unit vector $\mathbf{d}$. The integration over the whole set $D_A$ of relative chain lengths $n$ available in the direction $\mathbf{d}$ further yields the free energy of chains in this direction as

$$\psi^d = \int_{D_A} N(n, \bar{r}) \psi_p(n, \bar{r}) dn.$$  \hspace{1cm} (3)

The network evolution concept postulates aggregate-polymer debonding and network rearrangement as two simultaneous processes \cite{39}. In the course of deformation, short polymer chains slide on or debond from the aggregates. Under unloading, the debonded chains do not reattach back to the aggregates. Thus, the length of the shortest available chain in the deformed subnetwork is obtained by $n_{min}(\lambda^d m)$ where $\lambda^d m$ denotes the maximal microstretch previously reached in the loading history. Accordingly, the set of available relative lengths of chains bounded to aggregates in the direction $\mathbf{d}$ is given by $D_A(\lambda^d m) = \{n | n_{min} \leq n \leq n_{max}\}$.

Assuming the isotropic spatial distribution of polymer chains in all directions, the macroscopic energy of the PP network is obtained by

$$\Psi_{PP} = \frac{1}{A_s} \int_S \psi^d d\mathbf{u},$$

where $A_s$ represents the surface area of the microsphere $S$, and $d\mathbf{u}$ is the unit area of the surface with the normal direction $\mathbf{d}$.

**CP network.** In order to express $\Psi_{CP}$, the CP network is further decomposed into a number of subnetworks equally distributed in all spatial directions. Each subnetwork is then
considered as a directional representation of the CP network and can only be subjected to uniaxial tension (see Fig. 3).

Experimental observations show that samples made from the same compound are mechanically equivalent although the arrangement of filler aggregates in their micro-structures might be different. Accordingly, one can conclude that the mechanical behavior of the macroscale network is not considerably influenced by the microscale arrangement of its aggregates, provided that the filler content and the aggregation procedure are the same [40].

Accordingly, we assume a regular distribution of aggregates in the rubber matrix in order to assign a cell to each aggregate. The so-obtained idealized CP subnetwork (see Fig. 4) has a homogeneous and ordered distribution of aggregates inside. It is then meshed and subdivided into a finite number of cubic microcells of a constant volume. Each microcell is connected to the CC network by CP chains and linked to the PP network by its aggregate. The aggregate inside the cell is connected to the CC network by cross-links of its polymer chains and is moved and placed on the cell wall. Thus, an idealized cell is bonded to the CC network through its walls.

(3) Aggregates are placed in the middle of the cell.
(4) The number of CP chains inside the cell varies and depends on the size of the aggregates.
(5) CP chains inside the cell are considered to be of the same size [20].
(6) The numbers of polymer chains on both sides of the cell are identical.

In the following, we utilize the subscripts \( \bullet_p, \bullet_\xi, \bullet_c \) for nonkinematic quantities related to the specific constituents of the CP subnetwork, namely polymer chains, filler aggregates, and network cells, respectively. \( n_\bullet \) and \( N_\bullet \) denote, respectively, the number of constructing elements in a constituent and the number of these constituents per unit volume of rubber. \( \psi_\bullet \) and \( F_\bullet \) represent the strain energy of and the force applied to a constituent per its unit volume, respectively.¹

### A. Elasticity of the aggregate

Generally, colloidal clusters appear in form of complex geometrical structures, which can be described by the correlation length \( \zeta \), the fractal dimension \( d_f \), and the particle diameter \( l_c \). The aggregate correlation length \( \zeta \) can be considered as the average distance between two arbitrary points on the surface of the cluster [41]. The correlation length is related to the number of particles in the aggregate \( n_A \) by

\[
\psi_\bullet = \left( \frac{\zeta}{l_c} \right)^{d_f},
\]

where \( d_f \) is the fractal dimension of the cluster [42]. It reflects the compactness of the aggregate and depends mainly on the aggregation procedure [43].

Regardless of the cluster size, a backbone chain is necessarily formed inside it when loaded [44,45]. The backbone chain is a single chain of particles through which an external force is transmitted. The path and shape of this chain depend on the aggregation process and the loading direction. Similarly to Eq. (5), the number of particles in the backbone chain \( n_\xi \) is approximated by

\[
\psi_\bullet = \left( \frac{\zeta}{l_c} \right)^{d_f},
\]

where \( d_f \) denotes the fractal dimension of the backbone chain [42]. It characterizes the tortuosity of the backbone chain resulting from the fractal nature of clusters. The lower bound of \( d_f \) is 1, which corresponds to the straight path of the chain. The upper bound is given by \( \min \{d_f, 5/3\} \), where the value 5/3 corresponds to a self-avoiding walk chain.

¹Hereafter, the following font styles are used for scalar \( X \), vector \( \mathbf{X} \) and tensor values \( \mathbf{X} \).
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FIG. 4. (Color online) Schematic view of the CP subnetwork (a) before and (b) after the network rearrangement.

By decomposing the interparticle forces into centrosymmetric and tangential forces, the backbone chain can be modeled as a combination of elastic beams with the tensile spring constant $G$ and bending spring constant $\bar{G}$. Accordingly, the strain energy function of the backbone chain can be written by

$$
\psi_{\xi} = \frac{G}{2} \sum_{i=1}^{N} \Delta \phi_{ij}^2 + \bar{G} \sum_{i=1}^{N} \frac{1}{2l_i^2} \Delta l_i^2,
$$

(7)

where $\Delta \phi_{ij}$ denotes the difference in the angle between two successive bonds $i$ and $j$, $\Delta l_i$ the change in the length of bond $i$ between the current $\hat{l}_i$ and reference $l_i$ configurations. $N$ is the number of bonds in the backbone chain.

In order to describe the nonlinear behavior of an aggregate, one can define the overall elastic modulus $K_{\xi}(\hat{\lambda}_{\xi})$ as

$$
F_{\xi}(\zeta, \hat{\lambda}_{\xi}) = K_{\xi}(\hat{\lambda}_{\xi}) \zeta (\hat{\lambda}_{\xi} - 1) = \frac{1}{\zeta} \frac{\partial \psi_{\xi}}{\partial \hat{\lambda}_{\xi}},
$$

(8)

where $\hat{\lambda}_{\xi}$ represents the stretch of the aggregate in the direction of its backbone chain relative to the stress free state. $F_{\xi}$ denotes the force applied to the aggregate per unit referential volume. The elastic modulus $K_{\xi}$ can be formulated as a function of the aggregate kinematics (for details see [37,39]).

B. Elasticity of a polymer chain

In order to model polymer macromolecules, the concept of freely jointed chains (FJCs) is applied where the orientation of a segment is independent of the orientations and positions of adjacent segments. Consider a FJC with $n_p$ segments each of length $l_p$. Let $R$ and $r$ be vectors connecting the two ends of this chain in the reference and deformed configurations, respectively. Thus,

$$
r = F_p R,
$$

(9)

where $F_p$ is the microscale deformation gradient applied to the polymer chain. The lengths $R = ||R||$ and $r = ||r||$ represent the end-to-end distances of the chain in the reference and deformed configurations, respectively. Let us further introduce $R_0$ as the mean end-to-end distance of the polymer chain in the reference configuration. Thus, one can write

$$
R_0 = \sqrt{\bar{n_p}l_p}, \quad R_p = n_pl_p,
$$

(10)

where $R_p$ represents the contour length of the polymer chain.

The entropic free energy $\psi_p$ of a single polymer chain per unit referential volume is obtained on the basis of the non-Gaussian statistics as

$$
\psi_p(n_p, \hat{r}) = n_p K T \left( \frac{\bar{r}}{n_p} + \ln \frac{\beta}{\sinh \beta} \right),
$$

(11)

where $T$ stands for the temperature (isothermal condition is assumed) and $K$ is Boltzmann’s constant. The bar over a parameter $\bar{\text{•}}$ denotes its normalized value with respect to the segment length; e.g., $\bar{r} = \frac{r}{l_p}$. Further, $\beta = L^{-1}(\frac{\bar{r}}{n_p})$, where $L^{-1}$ denotes the inverse Langevin function. In the case of moderate and large deformations, the Taylor expansion appears due to its accuracy and simplicity to be the best approach for the approximation of the inverse Langevin function [46]. Accordingly, one has

$$
L^{-1}(x) = \sum_{i=0}^{20} C_i x^i,
$$

(12)

where the first 20 coefficients $C_i$ are given in Table I. The force on a single chain per unit referential volume can be obtained

FIG. 5. SEM micrographs of isolated aggregates in the polymeric solution. Two microcells with the same volume but different aggregates sizes are illustrated.
C. Governing equations

Let us represent the reference length and the stretch of a cell by \( L_0^c \) and \( \lambda_c \), and similarly, those of the aggregates by, respectively, \( L_\xi \) and \( \lambda_\xi \) (see Fig. 6). The spring constants of the aggregates and polymer chains are denoted by \( K_\xi \) and \( K_p \), respectively. Further, \( 2N_p \) stands for the number of polymer chains in a cell, while \( F_\xi \) and \( \lambda_\xi \) are the force and the yield force of an aggregate, respectively. In the following we subdivide all network variables into the subnetwork variables \( \mathcal{C}_N = \{ L_0^c, \lambda_c \} \) valid in the whole subnetwork, and the cell variables \( \mathcal{C}_c = \{ L_\xi, \lambda_\xi, K_\xi, K_p, N_p, F_\xi, \lambda_\xi \} \), valid only within their idealized cell.

Next, we have to derive the balance equations for the aggregate and the polymer chains inside the idealized cell [see Fig. 6(c)]. In the reference state, polymer chains are in the unperturbed state. In this state, no external stress is applied to the rubber network. It still has internal stresses that the aggregate volume \( V_\xi \) is balanced by a half of the polymer volume, we get for the reference state [see also Fig. 6(c)]

\[
\frac{1}{2} V_p N_p F_p(1, n_p) = V_\xi F_\xi(\xi, \lambda_\xi^{\text{res}}).
\]

In the current configuration kinematic relations (14) take the form

\[
L_\xi = \lambda_\xi \xi = \lambda_\xi \lambda_\xi^{\text{res}} \xi, \quad \lambda_p L_0^c = \lambda_\xi \xi_0 + 2 \lambda_p R_0.
\]

In view of Eq. (15) the balance equations are written in the current configuration by

\[
\frac{1}{2} V_p N_p F_p(\lambda_p, n_p) = V_\xi F_\xi(\xi, \lambda_\xi).
\]

The number of polymer chains \( N_p \) bonded to the aggregate surface can be approximated with respect to the active surface area of an aggregate \( (\xi, \lambda_c) \) by

\[
N_p = \alpha_p \left( \frac{\xi}{l_c} \right)^{\beta_p},
\]

where \( l_c \) represents the length of a particle, while \( \alpha_p \) and \( \beta_p \) are considered as material parameters.

The aggregate can further be considered together with a surrounding layer of the immobilized polymer (bond rubber) and approximated in a spherical form [40]. Thus,

\[
V_\xi = \frac{1}{6} \pi \xi^3, \quad V_c = (L_0^c)^3, \quad V_c = V_p + V_\xi.
\]

Accordingly, \( \mathcal{C}_c \) are evaluated for each idealized cell on the basis of the embedded aggregate size and the subnetwork parameters \( \mathcal{C}_N \).

IV. MECHANICS OF SUBNETWORKS

A. Yield of an aggregate

The yield behavior of filler aggregates depends on their geometry and the interactions between their particles. The yielding begins from the critical bond which can be identified based on applied tensile forces and bending moments. The yield force in the critical bond is then expressed by [47]

\[
F_y = F_y^c \left( \frac{2}{2 + \xi (1/2 + \xi)} \right),
\]

where \( F_y^c \) denotes the critical central force per unit bond volume in the absence of bending moments. Taking into account of

\[
\lambda_p = \lambda_c L_0^c.
\]

FIG. 6. (Color online) Schematic view of (a) a microcell, (b) an idealized cell, and (c) its representation by a set of nonlinear springs. The white chain inside the aggregate illustrates its backbone chain.

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account the magnitude of filler interactions and that the size of fillers used in elastomers is \( l_c \approx 8-500 \text{ (nm)} \) [40], one has \( \frac{1}{l_c} \gg \frac{Q}{U} \). Thus, in view of (6), Eq. (20) is reduced to
\[
F_y = F_{\gamma} = \frac{2}{2 + \frac{n_c}{2}} = \frac{2}{2 + \frac{n_c}{2}} V_c \lambda_{p} \lambda_{\circ} \lambda_{p}^0 \lambda_{r}^0 R_0, \tag{21}
\]
The yield force of the aggregate \( F_{\gamma} \) can then be assumed to be the yield force transmitted through the critical bond, thus,
\[
F_{\gamma} = F_{\gamma} \frac{V_b}{V_c} = F_{\gamma} \frac{V_b}{V_c} \frac{2}{2 + \frac{n_c}{2}}, \tag{22}
\]
where \( V_b \) is the volume of the bond. Accordingly, one can rewrite \( F_{\gamma} \) by
\[
F_{\gamma} = \frac{V_b}{V_c} = \tilde{F}_{\gamma} \left( \frac{1}{\xi} \right)^3, \tag{23}
\]
where \( \tilde{F}_{\gamma} = F_{\gamma} \frac{V_b}{V_c} \) and \( C \) is a constant. As reported in the literature (see, e.g., [48]) the magnitude of \( F_{\gamma} \) does not depend on the correlation length of the aggregate, but only on the particle type and the aggregation mechanism [49,50].

If an aggregate fails, its corresponding cell no longer contributes to the mechanical response of the subnetwork and is thus deactivated. The cell deactivation stretch \( \lambda_{\circ}^0 \) results from (16) as
\[
\lambda_{\circ}^0 = \lambda_{\circ} + 2 \lambda_{p} R_0, \tag{24}
\]
where the corresponding values of \( \lambda_{\circ} \) and \( \lambda_{p} \) are obtained from (17) by substituting the aggregate yield force (22) as
\[
F_{\gamma} = F_{\gamma} (\xi, \lambda_{\circ}^{\prime}, \lambda_{\circ}^{\prime}), \quad F_{\gamma} V_c = \frac{1}{2} V_p N_p F_p (\lambda_{p}, n_p). \tag{25}
\]
In view of (24), one can also calculate the size of the largest aggregate available in the reference configuration by
\[
\xi_{\text{max}} = \{ \xi | F_{\gamma} = F_{\gamma} (\xi, \lambda_{\circ}^{\prime}) \}. \tag{26}
\]

B. Re-aggregation and creation of soft bonds

Experiments on filled rubbers reveal a considerable stress softening between the first and subsequent loading cycles [51]. This behavior partly results from the recovery of filler aggregates due to the recreation of broken bonds between filler particles. During the recovery, the deformed parts of the broken aggregates come together and form new slightly weaker bonds [40]. The cyclic breakage and reformation of the bonds can be considered as an important source of the energy absorption and dissipation [40,52]. Although the form of a recreated aggregate differs from the original one, the mean geometrical parameters, such as the fractal dimension and the correlation length, are equal.

The recovery of damaged filler aggregates is a time-dependent process that requires thermal or mechanical activation energies [53] and governs the re-aggregation of a high fraction of broken aggregates during unloading. Our understanding of the influence of aggregate size on this procedure is limited to a few theories about the mechanism underlying the bond breakage and reformation [53,54].

Several studies assume that during unloading, the stress contribution of newly re-aggregated clusters (subject to compressive load) is considerably lower than the one of original aggregates (still subject to tensile load) and can thus be neglected [40,55]. In this case, the re-aggregated clusters can be assumed to form instantly at the end of unloading [56].

Following the re-aggregation model of Lin & Lee [56], we further extend their “zero strain recombination” concept by applying it to each direction, separately. Accordingly, we assume that the re-aggregation in any direction takes place when this direction becomes unstrained. Although the “zero strain recombination” concept does not provide a deep mechanical understanding of the re-aggregation process, it is widely used due to its simple implementation procedure.

Usually, interparticle bonds are classified into stiff and soft bonds according to the strength of filler-filler interactions. Based on the experimental measurement [40], one can consider the original bonds as stiff ones and the newly created bonds as soft ones. In the following, the yielding parameters of the soft bond will be denoted by an additional prime sign, e.g., \( F_{\gamma}^{\prime}, V_{b}^{\prime}, \lambda_{\circ}^{\prime}, \lambda_{p}^{\prime} \). In a recreated aggregate, only a small number of bonds are soft. For this reason, the elastic behavior of these aggregates is almost the same as of the original ones, although their yield forces considerably reduce. Once the yield forces of a recreated aggregate becomes smaller than the internal forces of the network in the reference configuration
\[
F_{\gamma}^{\prime} < F_{\gamma} (\xi, \lambda_{\circ}^{\prime}, \lambda_{p}^{\prime}), \tag{27}
\]
the aggregate will not be recreated anymore.

C. Aggregate size distribution

The mechanical response of the subnetwork in one direction is characterized by the aggregate size distribution in this direction. It can be evaluated by referring to Smoluchowski’s equation for the kinetics of the irreversible cluster-cluster aggregation of colloids (see, e.g., [57]). Empirically, the distribution is expressed by the logarithmic normal function [(40,58)] as follows:
\[
\Phi(\xi) = \frac{4}{g \xi} \left( \frac{\xi}{\xi_{\text{ref}}} \right)^{-2\Omega} \exp \left( -\left( 1 - 2\Omega \right) \frac{\xi}{\xi_{\text{ref}}} \right), \tag{28}
\]
where the exponent \( \Omega < 0 \) depends on the aggregation mechanism. For aggregates created by a diffusion limited cluster-cluster aggregation mechanism, \( 2\Omega \) is close to \(-0.44 \) [40]. Further, \( \xi \) represents the mean value of the aggregate size distribution while \( g \) is a normalization constant resulting from the condition
\[
\int_{0}^{\xi_{\text{ref}}} \Phi(\xi) d\xi = 1, \tag{29}
\]
related to the reference configuration.

D. Yield stretch of aggregates

In this section, we describe the size of deformed clusters available in the rubber matrix. Let
\[
\xi_{\text{max}} = \max \{ \xi^c, \xi^m \} \tag{30}
\]
be the size of the biggest available aggregate in the current configuration, where \( \xi^m \) and \( \xi^c \) denote the size of the biggest original and recreated aggregate available in the subnetwork, respectively. Since yielding of the original aggregates takes
Increasing amplitude. The stress-free states of the clusters are highlighted by circles.

One can write

$$\zeta^m := \bar{\zeta}^m (\lambda^m),$$

where

$$\lambda^m = \max_{\tau \in (-\infty, t]} \lambda_\zeta(\tau)$$

is the maximal microstretch previously reached in the loading history $\lambda_\zeta(\tau)$ of the aggregate while $\tau$ denotes time (see Fig. 7).

Substituting (31) into (26) further yields the following relation for $\lambda^m$, $\tilde{\lambda}^m$ of the aggregate while $\tilde{\lambda}_m$ is the maximal microstretch previously reached in the loading history $\lambda_\zeta(\tau)$ of the aggregate while $\tau$ denotes time (see Fig. 7).

$\zeta' := \bar{\zeta}' (\lambda')$, where $\lambda'$ is the maximal microstretch of the aggregate in the current loading cycle of $\lambda_\zeta$. In the case of an ideal cyclic loading (unloading to the stress-free state), $\lambda'$ can be formulated as (see Fig. 7)

$$\lambda' = \max_{\tau \in [0, \bar{\tau}]} \lambda_\zeta(\tau),$$

where

$$\bar{\tau} = \max_{\tau \in (-\infty, t]} \{ \tau | \dot{\lambda}_\zeta(\tau) = 0 \}$$

denotes the time when the last unloading cycle ends. Similarly to Eq. (33), for re-created aggregates one can calculate $\lambda'$ as

$$\bar{\zeta}' (\lambda') = \{ \zeta | \mathcal{F}_y = \mathcal{F}_\zeta (\zeta, \lambda', \lambda'_m) \},$$

Finally, Eq. (30) can be rewritten as

$$\zeta_{\max} = \max \{ \bar{\zeta}' (\lambda'), \bar{\zeta}^m (\lambda^m) \} := \tilde{\zeta}_{\max} (\lambda'_m, \lambda'_r).$$

E. Yield stretch of microcells

In this section, we further describe the active cells on the basis of the stretch applied to them and their aggregates. As discussed above, movements of the cross-links are assumed to be affine with the applied macrostretch. Consequently, the stretch $\lambda_\zeta$ applied on each cell is equal to the one applied on the corresponding subnetwork $\lambda$. The stretches of the aggregate and polymer chains are further abbreviated by

$$\lambda_\zeta := \dot{\lambda}_\zeta (\xi, \lambda), \quad \lambda_p := \dot{\lambda}_p (\xi, \lambda).$$

One can also write

$$\lambda^m := \dot{\lambda}^m (\xi, \lambda^m), \quad \lambda' := \dot{\lambda}' (\xi, \lambda'),$$

where

$$\lambda^m = \max_{\tau \in (-\infty, t]} \lambda(\tau), \quad \lambda' = \max_{\tau \in [0, \bar{\tau}]} \lambda(\tau)$$

in view of (32) and (35). Consequently, by virtue of (33) and (36), one can further rewrite (37) in terms of $\lambda^m$ and $\lambda'$ as

$$\zeta_{\max} = \max \{ \bar{\zeta}' (\lambda'), \bar{\zeta}^m (\lambda^m) \} = \tilde{\zeta}_{\max} (\lambda^m, \lambda').$$

Similarly, by inserting Eq. (38) into (17), one gets

$$F_c = \frac{V_c}{V_c} F_c (\zeta, \dot{\lambda}_c) = \dot{F}_c (\zeta, \lambda).$$

F. Subnetwork energy

The mean force $\langle F_c \rangle$ and the energy $\psi_c$ of a cell in a subnetwork can be formulated in terms of the probability density function $\Phi(\xi)$ by

$$\langle F_c \rangle = \int_0^{\xi_{\max}} \dot{\mathcal{F}} (\xi, \lambda^m) \Phi (\xi) d\xi,$$

$$\psi_c (x) = \int_1^x \langle F_c \rangle L^0 d\lambda.$$

Finally, the energy of the subnetwork in the direction $d$ is obtained as

$$\psi_{\text{sub}} = N_c \psi_c \left( \frac{d}{\lambda} \right),$$
CONSTITUTIVE MODELING OF THE MULLINS EFFECT

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FIG. 8. (Color online) Stress-stretch behavior of (a) all three networks CC + CP + PP, (b) CP network that accounts for the hysteresis, and (c) CC + PP networks that accounts for the idealized Mullins effect.

where \( N_c \) denotes the mean number of cells in the subnetwork. It is considered to be a material parameter.

V. TRANSITION TO THE MACROSCALE

A. 3D generalization

Using the above results we proceed to formulate the macroscopic energy of the three-dimensional network. The virgin rubber network is initially homogeneous and isotropic. The strain energy of the network is obtained as the sum of the energies of single subnetworks in different spatial directions. Applying an isotropic spatial distribution (idealized cells are spread equally in all directions), we write

\[
\Psi_{\text{CP}} = \frac{1}{A_s} \int_S d \Psi_{\text{sub}} \cdot d u,
\]

where \( A_s \) represents the surface area of the unit sphere. The integration is carried out numerically by

\[
\Psi_{\text{CP}} \approx \sum_{i=1}^{k} w_i d_{\text{sub}} \Psi_{\text{cp}} w_i, \tag{46}
\]

where \( w_i \) are weight factors corresponding to the collocation directions \( d_i \) \((i = 1, 2, \ldots, k)\). A set of \( k = 45 \) integration points on the half sphere is chosen [60], which was found to ensure the best trade-off between computational efforts and the numerical error due to the induced anisotropy [61].

B. Final formulation

The incompressibility condition

\[
\det F = 1 \tag{47}
\]

can then be written as

\[
T = \frac{\partial \Psi_{\text{CC}}}{\partial F} + \frac{\partial \Psi_{\text{PP}}}{\partial F} + \frac{\partial \Psi_{\text{CP}}}{\partial F} - p F^{-T}, \tag{48}
\]

where \( F \) denotes the macroscale deformation gradient and the unknown parameter \( p \) can be determined from the equilibrium and boundary conditions. The contributions of the CC and PP networks \( \frac{\partial \Psi_{\text{CC}}}{\partial F} \) and \( \frac{\partial \Psi_{\text{PP}}}{\partial F} \) have already been derived in the context of the network evolution model [36,39]. Here, we mainly focus on the stress contribution of the CP network

\[
T_{\text{cp}} = \frac{\partial \Psi_{\text{CP}}}{\partial F}. \tag{49}
\]

Using Eq. (46), one obtains

\[
\frac{\partial \Psi_{\text{CP}}}{\partial F} = \sum_{i=1}^{k} w_i \frac{d_{\text{sub}}}{d_{\text{sub}}} \frac{d_{\text{cp}}}{d_{\text{cp}}} \frac{d_{\text{cp}}}{d_{\text{cp}}}, \tag{50}
\]

where \( d_{\lambda} \) and \( d_{\chi} \) denote the micro- and macrostretches in the direction \( d_i \), respectively. Since the strain decomposition is applied only within the subnetworks, the micro- and

FIG. 9. (Color online) A cross-shaped specimen in the virgin and deformed state. Due to slits a homogeneous strain distribution is achieved within the measurement area as shown in the right figure.
TABLE II. Compound specifications of the rubber sample used in the cross-shaped specimen.

<table>
<thead>
<tr>
<th>Compound</th>
<th>phr</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polychloroprene (CR)</td>
<td>100</td>
<td>1210</td>
</tr>
<tr>
<td>Carbon black (N330)</td>
<td>50</td>
<td>1800</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>2</td>
<td>990</td>
</tr>
<tr>
<td>Processing aids</td>
<td>1.5</td>
<td>1230</td>
</tr>
<tr>
<td>Activator</td>
<td>2</td>
<td>3600</td>
</tr>
<tr>
<td>Cross-linker</td>
<td>5</td>
<td>2000</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>2</td>
<td>970</td>
</tr>
</tbody>
</table>

The macrostretches of the CP network are set equal to each other \( \lambda_i = \lambda \). Equation (50) can further be simplified by means of the following identity:

\[
\lambda = \sqrt{\frac{d}{d_i}} \Rightarrow \frac{1}{2} \frac{\partial d_i}{\partial F} = \sqrt{2} F(d \otimes d),
\]

(51)

where \( C = F^T F \) is the right Cauchy-Green tensor. Thus, Eq. (49) finally gives

\[
T_{cp} = \sum_{i=1}^{k} \tilde{T}_{cp} (d_i) \frac{w_i}{d_i} F(d_i \otimes d_i) - \rho F^{-T},
\]

(52)

where

\[
\tilde{T}_{cp}(x) = N_c L_c^0 \int_{\lambda_{max}(x', \lambda)}^{\lambda(x', \lambda)} \tilde{F}_c(\xi, \lambda) \varphi(\xi) d\xi.
\]

(53)

The contribution of the CP network to the overall stress response of the filled elastomer under cyclic loading with increasing amplitude is illustrated in Fig. 8. There, the stress-stretch curves of the CP network resulting from (52) are shown separately from the joint response of the CC and PP networks. It is seen that the CP network not only introduces the hysteretic behavior but also affects the stress softening in the first cycle due to the transformation of the original clusters to the recreated ones.

![Graphs](a) and (b) showing experimental stress-stretch diagrams for different directions.}

VI. MODEL EVALUATION

A. Experiment

A cross-shaped specimen made from 50 phr carbon black filled polychloroprene rubber (CR) was used (see Fig. 9). The exact material composition is given in Table II. The filler concentration in the sample is almost 50% by mass and 24% by volume (\( C \approx 0.2 \)). The experiment was performed at room temperature with the strain rate of 40% per minute. Experiments at lower strain rates did not reveal any considerable changes in the inelastic effects [51].

The specimens were loaded by a spindle-driven two-pillar universal tensile test machine that provides a constant clamping force, which is important for the measurement reproducibility [8]. Moreover, fast clamping and unclamping procedures reduce the influence of time-dependent effects, as for example relaxation. Stretches in the measurement area were registered by an optical measuring system.

The experimental procedure was as follows: The virgin specimen was subjected to loading-unloading cycles of uniaxial tension (\( x \) direction) with increasing stretch amplitudes of 1.15, 1.30, 1.45, 1.60, and 1.75. At each stretch amplitude, five cycles were conducted. After unloading to the stress free state, the sample was unclamped and reclamped again for the consequent loading in the orthogonal direction (\( y \) direction). Although the new configuration has some residual strains from the previous loading cycles, it is considered as the reference configuration for the loading in the \( y \) direction. Next, the above described loading procedure was repeated in the \( y \) direction.

The results are depicted in terms of nominal stress \( T \) versus stretch \( \chi \) in Fig. 10. The difference between the first and the subsequent cycles indicates the classical Mullins effect. One can also observe considerable permanent set both in \( x \) and \( y \) directions.

![Graphs](a) and (b) showing experimental stress-stretch diagrams for different directions.}
TABLE IV. Fitting parameters of the three-network model for 50 phr CR.

<table>
<thead>
<tr>
<th>Param. Description [CP Network]</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean size of the aggregates $\bar{\zeta}$</td>
<td>225 (nm)</td>
</tr>
<tr>
<td>Exponent of the aggregate size distribution $\Omega$</td>
<td>$-18.13$</td>
</tr>
<tr>
<td>Tensile yield force of an original particle-particle bond $\tilde{\sigma}_c$</td>
<td>535 (N)</td>
</tr>
<tr>
<td>Tensile yield force of a recreated particle-particle bond $\tilde{\sigma}'_c$</td>
<td>535 (N)</td>
</tr>
<tr>
<td>Parameters governing the number of polymer chains connected to an aggregate $N_p$ (18)</td>
<td>6, 1.15</td>
</tr>
<tr>
<td>Size of an idealized cell $L_c^0$</td>
<td>500 (nm)</td>
</tr>
</tbody>
</table>

[CC + PP Network]

<table>
<thead>
<tr>
<th>Param. Description [CC + PP Network]</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normalized active surface area of fillers $\kappa$</td>
<td>21.54</td>
</tr>
<tr>
<td>Distribution variance of the aggregate size $\nu$</td>
<td>1.0046</td>
</tr>
<tr>
<td>Average interparticle distance in the reference state $\bar{R}$</td>
<td>9.53</td>
</tr>
<tr>
<td>Normalized length of the longest available chain in the CC network $n_{\text{max}}$</td>
<td>37.01</td>
</tr>
<tr>
<td>Normalized number of active chains in the PP network $N_i KT$</td>
<td>1.28 (N m)</td>
</tr>
<tr>
<td>Normalized number of polymer chains in the CC network $N_c KT$</td>
<td>0.034 (N m)</td>
</tr>
<tr>
<td>Normalized length of polymer chains in the CC network $n_c$</td>
<td>100.6</td>
</tr>
</tbody>
</table>

y direction. The difference in stress-stretch curves between these directions is due to the anisotropy induced by the initial loading in $x$ direction.

B. Experimental Evaluation

In order to validate our model in comparison to the experimental results the following procedure was utilized.

![First cycle in x-direction](image1)

![First cycle in y-direction](image2)

![Subsequent cycles in x-direction](image3)

![Subsequent cycles in y-direction](image4)

FIG. 11. (Color online) Nominal stress versus stretch in uniaxial tension cycles in $x$ (left) and $y$ direction (right): comparison of the experimental data with the model predictions. The first (top graphs) and subsequent cycles (bottom graphs) are shown separately.
First, the material parameters given in Table III were set to the measured values given by [39,40,62]. Then, the model was fitted to the experimental data discussed above by 14 parameters listed in Table IV. As it can be seen, all these parameters have clear physical meaning.

Hysteresis in the first cycle is governed by both the CC and CP networks while in the second cycle only by the CP network. This allows us to evaluate first the parameters of the CP network by fitting the model to the experimental data on the second loading cycle [see Figs. 10(a) and 10(b)]. In the second step, the material constants corresponding to the CC and PP networks are obtained from the experimental data on the first loading cycle where the contribution of the CP network is eliminated [Fig. 10(c)]. The fitting is performed by using the Levenberg-Marquardt algorithm.

For the fitting, always the first and the second loading cycle up to the stretch amplitude 1.6 were used. Good agreement with other loading cycles was latter obtained automatically. The least-squares residual between the model predictions and the experimental data was minimized by means of the Levenberg-Marquardt algorithm.

The fitted values of the material parameters are given in Table IV while the corresponding stress-stretch curves are plotted in Fig. 11 against the experimental diagrams for the first and second loading cycles in the x and y directions. Good agreement of the model predictions with the experimental data in different loading cycles, directions, and for all stretch amplitudes can be observed. The three-network model successfully predicts all the aforementioned inelastic effects that are visible at large deformations of filled elastomers.

VII. CONCLUSION

A micromechanical constitutive model is proposed in order to account for different inelastic features in the behavior of filled elastomers. The model extends the previously developed network evolution concept towards the description of the cyclic hysteresis. To this end, the elastic strain energy, breakage, and recreation of aggregates previously considered as rigid are taken into account by introducing a new network in addition to the classical concept of the network decomposition. The model provides a microscale description to the damage mechanism taking place inside filled rubbers. A relatively small number of fitting parameters and the simple fitting procedure that requires only two loading cycles make the model a proper choice for further FE implementations. The efficacy and accuracy of the proposed model is confirmed in comparison with experimental results for different loading cycles and different loading directions.

ACKNOWLEDGMENTS

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