Mullins effect in polyethylene and its dependency on crystal content: A network alteration model

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ABSTRACT

This contribution is focused on the Mullins effect in polyethylene. An ultra-low-density polyethylene with 0.15 crystal content, a low-density polyethylene with 0.3 crystal content and a high-density polyethylene with 0.72 crystal content are subjected to cyclic stretching over a large strain range. Experimental observations are first reported to examine how the crystal content influences the Mullins effect in polyethylene. It is found that the cyclic stretching is characterized by a stress-softening, a hysteresis and a residual strain, whose amounts depends on the crystal content and the applied strain. A unified viscohyperelastic-viscoelastic-viscoplastic constitutive model is proposed to capture the polyethylene response over a large strain range and its crystal-dependency. The macro-scale polyethylene response is decomposed into two physically distinct sources, a viscoelastic-viscoplastic intermolecular part and a viscohyperelastic network part. The local inelastic deformations of the rubbery amorphous and crystalline phases are considered by means of a micromechanical treatment using the volume fraction concept. Experimentally-based material kinetics are designed by considering the Mullins effect crystal-dependency and are introduced into the constitutive equations to capture the experimental observations. It is shown that the model is able to accurately reproduce the Mullins effect in polyethylene over a large strain range. The inherent deformation mechanisms are finally presented guided by the proposed constitutive model.

1. Introduction

Polyethylene (PE) is the most common thermoplastic used in a large number of biomedical products, e.g. surgery implants, prosthetic joint, tubing, shunts, catheters, etc. (Ramakrishna et al., 2001; Kyomoto et al., 2012; Ratner et al., 2013). At the microscopic scale, PE has a semi-crystalline microstructure in which the ordered region is formed of crystallites interspersed with amorphous regions. At the macroscopic scale, the PE mechanical response is extremely nonlinear and time-dependent for which the most representative phenomena are stress relaxation, creep, and when subjected to cyclic loading the behavior is characterized by the appearance of hysteresis phenomena and the mechanical properties deterioration. Besides, under in-service conditions large strains may be locally reached in PE-based biomedical products design. The PE macro-scale response is governed by its microstructure features, the most basic being the crystal content. The crystal content in PE is ranged from about 70% down to a few percent only (Peacock, 2000), which confers to the material a wide range of behavior type, from thermoplastic to elastomeric one (Ayoub et al., 2011a; Abdul-Hameed et al., 2014a, 2014b). Development of sophisticated predictive constitutive models, in connection with semi-crystalline microstructure and deformation mechanisms, is of prime importance for design PE-based products.

The knowledge of the deformation mechanisms in semi-crystalline polymers is substantial under monotonic loading paths (Seguela et al., 1998a, 1998b; Bartczak, 2005; Bartczak and Kozanecki, 2005; Kazmierczak et al., 2005; Boulahia et al., 2009; Bartczak and Galeski, 2010; Galeski et al., 2010; Patlazhan and Remond, 2012; Rozanski and Galeski, 2013). The non-deformed molecular network of the amorphous phase consists of chains, entangled physically and chemically,
randomly distributed thus assumed to be isotropic. In the early stage of deformation until yield point, the stress-strain relationship of the semi-crystalline polymer is governed by the chains interaction in the amorphous phase and by the plastic deformation in the crystalline phase: The chains of the amorphous phase are first stretched and some chains unfold and weak bonds between them break-up. This mechanism is then followed by rotation of chains in the crystalline lamella that reorient in the maximum principal stretch direction. At large strains, the macro-scale response is governed by the alignment of chains in the maximum principal stretch direction: The crystalline lamellae separate into crystalline block segments and finally, the crystalline block segments and the amorphous linking reorient along the maximum principal stretch direction leading to a significant strain-hardening before the chains reach their extensibility limits and break (Elmeguenni et al., 2013). In the plastic regime, the principal stretch along the chain direction tends to enhance chain elongation and reduce the distance between neighboring chains, and as a consequence to increase the number of entanglements and thus the stiffness. By contrast, the principal stretch perpendicular to the chain direction leads to increase the distance between neighboring chains and decrease the number of entanglements.

Under cyclic stretching, the semi-crystalline polymers exhibit different macro-scale characteristics which are common with elastomeric-like materials as illustrated in Fig. 1: (i) A deformation-induced stress-softening occurring after unloading, (ii) a hysteresis (i.e. a difference between unloading and reloading paths) illustrating the viscoelastic response, (iii) a residual strain for which the stress is zero at unloading. This set of phenomena is conventionally referred now to as the Mullins effect and it is well-documented in a multitude of studies for the elastomeric materials (Bouasse and Carrière, 1903; Mullins, 1948, 1969; Buche, 1961; Harwood et al., 1967; Markmann et al., 2002; Chagnon et al., 2006; Dargazany and Iskovev, 2009; Ayoub et al., 2011b, 2014; Dargazany et al., 2014; Ovalle-Rodas et al., 2014, 2016). The Mullins effect in elastomeric materials is mainly associated to molecular network degradation and its modeling is generally idealized without hysteretic and residual strain. In the case of semi-crystalline polymers, very few studies exist (Drozdov, 2009; Drozdov et al., 2013; Wang et al., 2015). The hysteresis may be trivially attributed to molecular network reorganization during unloading and reloading. The first hysteresis loops, that form in the stress-strain response between unloading and reloading, are “open”, which means that the strain at unloading is considerably different than that at loading. Nevertheless, after few cycles the hysteresis loop “closes” (Nguyen et al., 2013). During unloading, the plastic deformation occurring in the crystal phase is permanent, while the deformation in the amorphous phase is partially recoverable. The recovered strain depends on the network and microstructure properties, e.g. chains size and entanglement, amorphous phase content, etc. (Yashiro et al., 2010). The recovered strain in the amorphous phase during unloading leads to a new molecular network configuration and may also induce crystal block segment reorientation in addition to the one induced by the maximum principal stretch. The uncoiling of the crystalline lamella creates new physical linkages. The change of the number of entangled points reversely changes the number of segments in a single chain. The relation between entangled points and segment number in a single chain has a great impact on unloading deformation behavior. During cyclic deformation, the chains distribution and orientation evolve and lead to a new equilibrium molecular network state. At certain strain levels, short chains reach their extensibility limits and break while the longer chains start to deform or stay in relaxed configuration (Ayoub et al., 2014).

Fig. 1. Typical cyclic stress-strain response illustrating the Mullins effect in PE.
2. Experiments

Mechanical tests were performed to investigate how the crystal content influences the main features of the PE cyclic response.

2.1. Materials and specimen

The studied PE materials consist of a Ziegler-Natta high density ethylene-hexene copolymer (HDPE) from Total Petrochemicals, a linear low density ethylene-octene copolymer (LDPE) and an ultra-low density ethylene-octene copolymer (ULDPE) from DOW Chemicals, both issued from metallocene catalysis. The molecular characteristics of the PE materials provided by the manufacturers are given in Table 1. In summary, the highest average molecular weight $M_w$ is found for the HDPE and the lowest is found for the LDPE, $M_w = 150$ kDa for ULDPE, $M_w = 104$ kDa for LDPE, and $M_w = 174$ kDa for HDPE. The HDPE is manufactured by Total Petrochemicals at low temperatures and pressures using Ziegler-Natta catalysts, the high density $\rho = 0.959$ g/cm$^3$ results from the lack of branches allowing the polymer chains to pack closely together. The LDPE and ULDPE are both manufactured by DOW Chemicals at high temperatures and pressures from gaseous ethylene-octene using metallocene catalysis yielding to both long and short branches polymer structure. The crystallinity of the PE materials was determined by differential scanning calorimetry (DSC) analysis. The crystal weight fraction was obtained from the ratio of the heat of fusion measured by means of a Q100-apparatus from TA Instruments to the theoretical heat of fusion for 100% crystalline PE. The value in volume was calculated by multiplying the crystal weight fraction by the ratio between the material density and the crystal density (1.0 g/cm$^3$).

PE pellets were transformed by compression molding at 180 °C into 1 mm thick sheets and slowly cooled to room temperature in order to avoid residual thermal stresses generated during cooling. Although material isotropy is expected, the PE specimens were cut from the compression molded sheets along the same direction. The PE specimens are in the following dimensions: 28 mm in length and 8 mm in width. The deformation is localized in the central part of the specimen by imposing a curvature radius of about 120 mm.

2.2. Method

The intrinsic large inelastic deformation response of the PE materials was determined by means of a universal testing machine Instron-5800 connected to a non-contact optical extensometer (a CCD camera interfaced with a computer) for the local strain measurements. The technique has the advantage of reducing perturbation induced by classical extensometers and to maintain constant the local true axial strain rate throughout the test by regulating the cross-head speed of the testing machine. The applied force was measured during the tests using a standard load cell of 1 kN. The true axial stress was calculated by dividing the value of the force with the actual specimen cross-section recorded by the video setup. Cyclic tests at different pre-strains were conducted at a constant true axial strain rate of $10^{-3}$ s$^{-1}$ and at room temperature. The true axial strain was ramped to a prescribed value and then ramped down to zero true axial stress followed by a reloading.

Table 1

<table>
<thead>
<tr>
<th>Materials</th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\chi_w$ (%)</th>
<th>$\chi_v$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULDPE</td>
<td>75</td>
<td>150</td>
<td>0.870</td>
<td>17.4 ± 0.3</td>
<td>15.1 ± 0.2</td>
</tr>
<tr>
<td>LDPE</td>
<td>50</td>
<td>104</td>
<td>0.902</td>
<td>33.3 ± 0.8</td>
<td>30.0 ± 0.7</td>
</tr>
<tr>
<td>HDPE</td>
<td>14</td>
<td>174</td>
<td>0.959</td>
<td>75.5 ± 0.8</td>
<td>72.4 ± 0.8</td>
</tr>
</tbody>
</table>

Fig. 2. Cyclic stress-strain responses of PE materials: (a) HDPE, (b) LDPE, (c) ULDPE; insets present AFM images of surface morphology of each PE material (1 μm in each side).
2.3. Experimental results

In this subsection, various phenomena observed in the PE cyclic behavior are presented. Fig. 2 illustrates the Mullins effect in PE and its crystal-dependency. It represents the stress-strain curves of the PE materials submitted to one cycle tensile loading with increasing maximum strain. The initial morphologies of the three PE materials are also provided as insets in the figure in order to evidence the transition from dense crystal packing morphology to a morphology consisting of bundle-like crystals embedded in the rubbery amorphous matrix. Under monotonic stretching, similar to many ductile thermoplastic polymers, PE exhibits a highly nonlinear stress-strain relationship. A global view at these results indicate that the plastic yielding and the strain-hardening response are greatly influenced by the crystal content, also because the amorphous phase is in the rubbery state at room temperature. Therefore, the PE response evolves from a typical thermoplastic to a typical elastomeric by decreasing the crystal content (Ayoub et al., 2011a; Abdul-Hameed et al., 2014a, 2014b). The HDPE mechanical response is successively characterized by a stiff initial response, a viscoelastic response with a constant initial slope that gradually decreases until the yield stress, a gradual strain-hardening and finally a significant strain-hardening at very large strains. The ULDPE mechanical response is characterized by low stress levels compared to the HDPE stress, and exhibits which seems to be a yield-like event and a largely predominant strain-hardening which is typical of thermoplastic elastomers. The ULDPE macroscopic behavior is mainly attributed to the rotation and sliding of chains in the amorphous phase followed by the alignment of chains in the direction of loading, while the crystalline phase contribution to the overall mechanical response is slight. The decrease in the ULDPE strain-hardening slope can be attributed to the presence of a higher number of longer chains compared to the HDPE material. The LDPE mechanical response exhibits an obvious yield-like event and its large strain deformation is dominated by the molecular orientation of the rubbery amorphous phase. When unloaded at different pre-strains, the PE mechanical response is initially linear and then becomes highly nonlinear for all pre-strains leading to the formation of the hysteresis loop with reloading. The difference between unloading and reloading paths is related to the amount of energy that is dissipated during a cycle. The response recaptures the same path as that corresponding to the monotonic one when the strain exceeds the maximum strain previously applied. A highly nonlinear unloading leads to a decrease in residual strain in the LDPE and ULDPE materials compared to the HDPE material when unloaded at the same pre-strain. A considerable decrease in the nonlinearity of the unloading as the pre-strain increases can be pointed out in HDPE. Indeed, at higher pre-strains, the viscoelastic stage becomes less nonlinear under unloading tending to close-up the hysteresis loop with reloading.

In order to evaluate the stress-softening beyond the Mullins effect, Fig. 3 presents the stress-strain curves of the PE materials submitted to several cycles at a certain pre-strain; the maximum strain applied on each PE material is different in the figure for the sake of clarity. The cyclic stress-strain response results from a massive structural rearrangement accompanied by widely diverse deformation mechanisms modifying the original structure to another one at each new cycle of the cyclic loading. Stress-softening, residual strain and energy dissipation are reported as a function of the cycle number in Figs. 4 and 5. Because of the Mullins effect, the first to second cycle transition exhibits the highest stress decrease. The stress tends then towards a stabilized value which depends on the strain level and the crystal content. The softening magnitude increases with the increasing strain level and with the increasing crystallinity. Similar observations are reported on the stress-softening behavior of rubbers containing different fractions of fillers (Ovalle-Rodas et al., 2016). During the first few cycles on the same pre-strain, the stress-softening saturation tends to close-up the hysteresis loop and a repeatable response is observed. As a consequence of the permanent microstructure reorganization, the strongest residual strain and dissipated energy for the same strain level appear after the first load. Under further cyclic loading, the PE materials tend towards a kind of stabilized state for which there is no significant change in residual strain and dissipated energy. The dependence regarding the applied strain-level and the crystal content is also evidenced in these plot.

3. Viscohyperelastic-viscoelastic-viscoplastic constitutive model

In order to capture the PE mechanical response over a large strain range, a constitutive model, satisfying the continuum mechanics rules within the large inelastic deformation kinematics framework, is proposed. The low-strain mechanical response of PE is predominantly associated with the interactions between chains in the crystalline and amorphous domains, while the large-strain mechanical response is mainly related to the extension of chains. The inelastic deformation response of the semi-crystalline PE material may be modeled by assuming that the deformation mechanisms are split into an intermolecular resistance and a molecular network stretching/orientation resistance, as schematically represented in Fig. 6. The intermolecular resistance captures the initial response and the yielding rate-dependence due to the isotropic resistance to deformation resulting from intermolecular barriers both to chain-segment rotation in the amorphous phase and to crystallographic shear in the crystalline phase. The molecular network resistance reproduces the anisotropic strain-hardening response at large strains due to stretching and orientation. From a micromechanical point of view, the semi-crystalline PE material may be seen as a two-phase composite constituted by crystalline and rubbery amorphous domains. The macro-scale response is then obtained by a micromechanical treatment. The complex couplings existing between semi-crystalline microstructure and macro-behavior may be considered using advanced micromechanics-based approaches (Anoukou et al., 2014). Considering finite strain effects, a volume fraction concept (Ayoub et al., 2010; Zaïri et al., 2010) is preferred in which the
interactions are taken into account without matrix-amplification inspired factor (Ovalle-Rodas et al., 2015). The two domains are supposed to participate to intermolecular interactions via the Taylor assumption, i.e. branches parallelism: amorphous stiffness and flow are in parallel with those of the crystalline phase.

Throughout the paper, vector and tensor quantities are represented with bold-face symbols, while scalars and individual components of vectors and tensors are written in italics. The prime ′′′ indicates the
which maps a material point from its initial position to its current position. The constitutive model being constructed with the Taylor assumption, the deformation gradients in the intermolecular configurational space are equal to the total deformation gradient:

\[ \mathbf{F} = \mathbf{F}_A + \mathbf{F}_B \]  

(1)

The Taylor assumption also prevails in the split of the intermolecular resistance into crystalline and amorphous parts:

\[ \mathbf{F}_A = \mathbf{F}_A \]  

(2)

in which the superscript \( i \) denotes the phase under consideration, crystalline \( c \) or amorphous \( a \).

Following the Lee (1969) elastic-viscoplastic decomposition or the Sidoroff (1974) viscoelastic decomposition, the deformation gradients can be further decomposed in a multiplicative manner into elastic (network) and viscoplastic (flow) parts:

\[ \mathbf{F}_i = \mathbf{F}_i^e \mathbf{F}_i^p \]  

(3)

in which the superscripts \( e, p, N \) and \( f \) denote the elastic, viscoplastic, network and flow parts, respectively.

The deformation gradients are further decomposed into stretch and rotation movements using the polar decomposition:

\[ \mathbf{F}_i^e = \mathbf{V}_i^e \mathbf{R}_i^e \]  

(4)

The rate kinematics are described by the velocity gradients:

\[ \mathbf{L}_i^e = \mathbf{F}_i^e \mathbf{F}_i^{e-1} + \mathbf{F}_i^p \mathbf{F}_i^{p-1} \]  

(5)

in which the dot denotes the time derivative.

The plastic and flow parts of the velocity gradients may be written as:

\[ \mathbf{L}_i^p = \mathbf{F}_i^p \mathbf{F}_i^{p-1} \]  

(6)

where \( \mathbf{D}_A^p \) and \( \mathbf{D}_B^p \) are the inelastic deformation rates and, \( \mathbf{W}_A^p \) and \( \mathbf{W}_B^p \) are the inelastic spin rates.

Nucleated within the amorphous phase between the crystalline lamellae, cavitation damage may involve in PE (Pawlak et al., 2014). A specified treatment (Zaïri et al., 2005a, 2008, 2011) is needed to take into account the inelastic volume change effects, which are ignored in the present model, i.e. \( \det \mathbf{F}_A^p = \det \mathbf{F}_B^p = 1 \). Assuming, the inelastic flow irrotational, i.e. \( \mathbf{W}_A^p = \mathbf{W}_B^p = 0 \), the relation (6) gives the evolution equations of the inelastic deformation gradients:

\[ \mathbf{F}_A^p = \mathbf{F}_A^p \mathbf{D}_A^p \mathbf{F}_A^{p-1} + \mathbf{F}_A^p \mathbf{F}_B^p \]  

(7)

in which the inelastic deformation rates will be defined below.

The elastic and network deformation gradients are then extracted from:

\[ \mathbf{F}_A^e = \mathbf{F}_A^e \mathbf{F}_A^{p-1} \]  

(8)

3.2. Model formulation

In what follows, the three-dimensional constitutive equations, expressing the inelastic stretching rate as a function of the stress in the material, are described for the two resistances. The total Cauchy stress in PE is given by the tensorial sum of the Cauchy stresses within the two resistances:

\[ \mathbf{T} = \mathbf{T}_A + \mathbf{T}_B \]  

(9)

3.2.1. Viscoelastic-viscoplastic intermolecular resistances

The semi-crystalline material is treated as a heterogenous medium by distinguishing amorphous and crystalline phases in the isotropic intermolecular response resulting from the elementary viscoelasticity and yielding mechanisms. The contribution of each phase is represented by a viscoelastic spring in series with a viscoplastic dashpot, capturing barriers both to molecular chain segment rotation in the amorphous phase and to crystallographic shear in the crystalline phase. The overall intermolecular resistance \( \mathbf{T}_A \) is captured by the following expression (Ayoub et al., 2011):

\[ \mathbf{T}_A = \chi^2 \mathbf{T}_A + (1 - \chi) \beta \mathbf{T}_A \]  

(10)

in which \( \chi \) is the crystalline volume fraction, \( \beta \) is a factor associated to the load-transfer of the amorphous phase between the crystallographic
segments, \( T_A \) and \( T_A' \) are the crystalline and amorphous intermolecular Cauchy stresses related to the corresponding stretch part of the elastic deformation gradient by the following constitutive relationship:

\[
T_A' = \frac{1}{J_F} C_I \ln(V')/\text{with} \ V' = F'/R_{\text{c}}^{-1}
\]  

(11)

where \( J_F = \det F \) is the elastic volume change, \( \ln(V') \) is the Hencky elastic strain, \( V_{eq}^F \) is the elastic stretch, \( R_{\text{c}}^F \) is the elastic rotation and \( C_I^F \) is the fourth-order tensor of elastic constants expressed, for an isotropic material, in terms of the Young's modulus \( E \) and the Poisson's ratio \( \nu \):

\[
(C_{ijkl}^F)_{	ext{conf}} = \frac{\nu \phi}{2(1 + \nu)} \left( \delta_{ij} \delta_{kl} + \frac{2
u}{1 - 2
u} \delta_{ik} \delta_{jl} \right)
\]  

(12)

where the term \( \delta \) is the Kronecker-delta symbol, \( \phi \) and \( \phi' \) are functions introduced to capture the change in the elastic stiffness under loading/unloading.

The function \( \phi' \) was introduced by Ayoub et al. (2010) to describe the recovery governed by the entropic back stress at large-strain during unloading:

\[
\phi' = \frac{1}{2} \nu \left( \frac{\phi'}{\nu} \right)^{\nu/n_i}
\]  

(13)

The function \( \phi' \) incorporates the nonlinear viscosity effects on the elastic part and the inelastic stresses are non-zero at all stages of loading. In the elastic regime, \( \phi' = 1 \) and it is close to zero when the inelastic flow is fully established. The terms \( \alpha_i \) and \( \beta_i \) are parameters, \( \nu_i \) is the maximum of a deformation measure and \( \delta_i \) is a deformation measure related to the network resistance:

\[
\sigma'_{\text{ck}}(t) = \max \left( \alpha_i \right) \tau(t) \text{and} \quad \alpha_i^N = \frac{\xi}{\delta_i}
\]  

(14)

in which the term \( \xi \) and \( \delta_i \) correspond to the inverse Langevin function (defined below) in the current and reference configurations, respectively.

The function \( \phi' \) is active at low-strain, from the elastic regime to the rollover to yield, and evolves according to isotropic, equilibrium and kinematic stresses (Colak, 2005):

\[
\phi' = 1 - \beta_i \left( \frac{x'}{r} \right)^{\nu_i}
\]  

(15)

The function \( \phi' \) incorporates the nonlinear viscosity effects on the elastic part and the inelastic stresses are non-zero at all stages of loading. In the elastic regime, \( \phi' = 1 \) and it is close to zero when the inelastic flow is fully established. The terms \( \alpha_i \) and \( \beta_i \) are parameters, \( r_i \) is the isotropic stress and \( \nu_i \) is the effective value of the difference between the equilibrium stress \( G' \) and the kinematic stress \( K' \):

\[
k' = \left( \frac{1}{2} (G' - K'), (G'' - K'') \right)^{1/2}
\]  

(16)

in which the dot denotes the tensor product: \( A \cdot B = \text{tr}(A^T B) \), \( A^T \) being the transpose of \( A \).

The viscoelastic strain rate tensor is expressed as:

\[
D_N^{(\nu)} = \nu \phi' \frac{T_A' - G'}{\sqrt{3} r_A'}
\]  

(17)

where \( r_A' \) is the effective value of the difference between the intermolecular Cauchy stress \( T_A' \) and the equilibrium stress \( G' \):

\[
r_A' = \left( \frac{1}{2} (T_A' - G'), (T_A' - G') \right)^{1/2}
\]  

(18)

The plastic shear strain rate \( \dot{\gamma}^{pl}_i \) is given by a power law depending on the earlier effective stress quantity (Colak, 2005):

\[
\dot{\gamma}^{pl}_i = \left( \frac{3}{2} \sqrt{3} \frac{r_A'}{D} \right)^{m_i}
\]  

(19)

where \( D \) is the drag stress and \( m_i \) is a viscosity parameter.

The viscoelastic stress \( K' \) is expressed in its deviatoric form as:

\[
K' = \frac{1}{\sqrt{2}} \left( V_{eq} \frac{T_A' - T_A'}{\sqrt{3} r_A'} + g' E_A - E_{\text{r}} \right) D_N^{(\nu)}
\]  

(20)

where \( E_{\text{r}} \) is the tangent modulus.

The equilibrium stress \( G' \) is expressed in its deviatoric form as:

\[
G' = \Psi \left( \sqrt{3} \frac{T_A'}{E_A} \right)^{1/2} \left( T_A' - G' - K' \frac{E_A}{r'} \right) + \left( 1 - \frac{\nu}{E_A} \right) K'
\]  

(21)

in which \( \Psi \) is a shape function that captures the rollover to yield:

\[
\Psi = \Psi'_i + \left( \frac{\gamma_i - \Psi'_i}{E(\xi)} \right) \text{and} \quad \Psi'_i = c_i \left( 1 + c_i \left( \frac{g'}{r' + k\xi + (\xi c_i)^2} \right) \right)
\]  

(22)

where \( c_i \leq c_i \) are parameters, \( g' \) and \( k' \) are the effective equilibrium and kinematic stresses, respectively:

\[
g' = \left( \frac{1}{2} G', G'' \right)^{1/2} \text{and} \quad k' = \left( \frac{1}{2} K', K'' \right)^{1/2}
\]  

(23)

3.2.2. Viscoplastic network resistance

The strain-hardening response is supposed to be dominated by molecular orientation rather than crystallographic orientation. The molecular network resistance is constituted by a nonlinear spring in series with a viscous dashpot. The nonlinear spring can be represented by a purely descriptive phenomenological approach (e.g. Zairi et al., 2005b, 2007; Pyrz and Zaïri, 2007) or a statistical approach (e.g. Treloar, 1975; Arruda and Boyce, 1993; Boyce and Arruda, 2000). The last one integrates in its formulation the molecular network properties and uses the extensibility limit of polymer chains as a deformation measure. The molecular network Cauchy stress \( T_b \) is expressed by the Arruda and Boyce (1993) statistically-based relationship:

\[
T_b = \frac{1}{3} \frac{n_k \delta}{J_B^b} \frac{\sqrt{N_r}}{\sqrt{\alpha_B}} \left( B^N - (\alpha_B) N \right) \mathbf{I}
\]  

(24)

in which \( J_B^b = \det F_b \) is the network volume change, \( \mathbf{I} \) is the identity tensor, \( n_k \) and \( N_r \) are the two network parameters: the average number of chains per unit volume (introduced in the rubbery modulus \( C = n_k \delta \) being the Boltzmann's constant and \( \delta \) the absolute temperature) and the average number of rigid links in a chain, respectively. The symbol \( \alpha \) denotes the inverse Langevin function: \( \alpha = (N_r^b / \sqrt{N_r}) \). The term \( \sqrt{N_r} \) represents the limiting extensibility of the polymer chains; if the chain stretch approaches this limit, the stress increases dramatically following the inverse Langvin function \( \alpha = (N_r^b / \sqrt{N_r}) \) given by a Padé approximation (Cohen, 1991):

\[
\alpha(x) = \frac{3}{2} - x^2 (1 - x^2)
\]  

(25)

Note that as \( \sqrt{N_r} \) approaches infinity, the relation (24) reduces to the classical Neo-Hookean model, involving no dramatic strain-hardening. The terms \( x_r^b \) and \( B^N \) are the stretch on each chain in the network and the left Cauchy-Green tensor, respectively:

\[
x_r^b = \left( B^N ight)^{1/2} \text{and} \quad B^N = (J_B^b)^{2/3} F_b (F_b)^T
\]  

(26)

In addition to the stretching and orientation process, a molecular relaxation process is included in the model formulation from the flow strain rate tensor \( D_b \) described by the following flow rule:

\[
D_b = \nu \phi' \frac{T_b}{\sqrt{2} \nu_b}
\]  

(27)

where \( \nu_b \) is the effective value of the Cauchy stress \( T_b \):

\[

\nu_b = \frac{1}{2} T_b - T_b^{1/3}
\]  

(28)

The flow shear strain rate \( \dot{\gamma}^{pl}_i \) is given by (Boyce et al., 2000):
\[
\dot{\lambda}_B^f = D \exp \left( - \frac{Q}{R^3} \frac{\tau_B}{\lambda_B^f - 1} \right)
\]  

(29)

In order to ensure numerical stability due to singularity at the beginning of the loading process where \( \lambda_B^f = 1 \), a perturbation coefficient \( \kappa = 0.01 \) is added to \( \lambda_B^f \) throughout our simulations. The terms \( D \) and \( Q \) are two viscosity parameters introduced because of the physics of chain relaxation, \( R \) is the universal gas constant and \( \lambda_B^f \) is given by:

\[
\lambda_B^f = \left( \frac{1}{3} \text{trace} \mathbf{B} \right)^{1/2} \quad \text{and} \quad \mathbf{B} = \mathbf{F}_B \mathbf{F}_B^T
\]

(30)

Our main aim is now to determine the model parameters and to design parameter kinetics in order to develop a plausible model for describing the PE material response under loading-unloading-reloading.

### 3.3. Experimentally-based material kinetics

#### 3.3.1. Model vs. cyclic data

Fig. 7 illustrates the initial semi-crystalline microstructure that consists in ordered regions formed of crystallites interspersed with randomly distributed amorphous chains. The deformation mechanisms responsible of the Mullins effect in PE can be correlated to those activated in elastomeric materials. Ayoub et al. (2011b) studied the deformation mechanisms activated under cyclic loading in elastomeric materials. They reported that for a given strain level and under cyclic loading, the mechanical behavior of an elastomeric material is different between the first cycle and the cycles that follow, which constitutes the first basic observation of the Mullins effect. This difference in the mechanical response is attributed to the rearrangement of the molecular network. Furthermore, chains reaching their extensibility limits break when stretched at a given strain level. Therefore, a new equilibrium state of the molecular network is reached when the sample is stress-free. As the entropy is lower than in the virgin network, a consequence of a more organized molecular network, the residual strain appears. Increasing the strain levels decreases the entropy and by consequence increases the intensity of the residual strain. Ayoub et al. (2014) accounted for the Mullins effect in elastomeric materials by considering the stress-softening, the hysteresis loop and the residual strain and their evolution as a function of the applied pre-strains in their constitutive model by identifying from the experimental results a network alteration kinetics. The evolution of the loading-unloading-reloading response, perceived by the presence of the residual strain and the hysteresis loop in PE, can be also attributed to the microstructure alteration. We suppose that the reported deformation mechanisms can be also active in PE. However, the deformation mechanisms in the amorphous and crystalline phases still need to be identified. Proposing a suitable evolution of the parameters of the amorphous and crystalline parts along with the network alteration kinetics allow the constitutive model to capture the stress-strain response under loading-unloading-reloading at
different pre-strains and help identifying the deformation mechanisms in the different phases.

Fig. 8 compares the simulated and measured stress-strain curves. It is satisfactory to observe that the constitutive model captures the Mullins effect over a large strain range. In particular, the ability of the constitutive model to reproduce the viscoelastic and viscoplastic dissipative mechanisms is shown. To capture the stress level and crystal content effects on the PE cyclic stretching features (stress-softening, hysteresis and residual strain), material kinetics, related to the network and intermolecular properties, are designed and plotted in Figs. 9–12. In what follows, the deformation mechanisms in PE associated to the Mullins effect are discussed guided by the proposed constitutive model.

3.3.2. Deformation mechanisms

We can explain the Mullins effect in PE by the scenario illustrated in Fig. 7. In the intent to describe the hysteresis loop and the residual strain, we consider that mainly shorter chains are active during loading while longer chains are active during unloading. The transmission in the activity between the longer chains to the shorter chains results in the hysteresis loop. The two network parameters affected by the network alteration are the average length of the network chains \( N_r \) and the average number of chains by volume unit \( C_r = n_k \beta \). Furthermore, as different chains, depending on their length, are contributing to the mechanical response under loading and unloading, therefore the rotation and the slipping of those chains will be affected, and thus an evolution of certain intermolecular parameters is necessary.

The evolution of the average number of chains during loading and unloading is given in Fig. 9. The difference in network resistance parameters may be attributed to the difference in average chain length related to the difference in molecular weights. The evolution of the average chain length \( N_r \) is related to the evolution of \( C_r \) as the evolution of these two network parameters is governed by the mass conservation law which indicates that the total number of monomers per unit volume remains constant \( C_r N_r = \text{constant} \). Fig. 9b shows a decrease in the values of \( C_r \) while decreasing strain level, which means that \( N_r \) is increasing with decreasing strain. Moreover, this evolution highlights clearly that under unloading the longer chains are mainly controlling the deformation as an increase in \( N_r \) means an increase in the average length of the active chains. Fig. 9a shows an increase in \( C_r \) with increasing strain, which also means that \( N_r \) is decreasing with increasing strain. We can confirm from those observations that short chains are controlling the deformation mechanisms under loading as an increase in \( C_r \) indicates a decrease in the average length of the active chains. Furthermore, it is worth noticing that the value of \( C_r \) is constant \( (C_r = C_{0r}) \) when we start the unloading and when we complete the reloading, indicating that the active chains during monotonic loading have intermediate length. Additionally, \( C_r \) will increase with increasing pre-strain level accounting for the chain scission mechanism (Belbachir et al., 2009).

As explained earlier, during reloading the chains align with the first principal stretch direction and try to resist deformation hence the number of entanglements between chains increases which is correlated to the increase of the density of chains proportional to \( C_r \). However, since there is no volume change and the smaller chains reach their limit of extensibility and chain breakage occurs hence there is a decrease in entanglement density. During unloading (retraction) the stored energy is released and contributes to chains that met their limit of extensibility retracting chains and recovering deformation. We suppose that the chain density decreases but the number of entanglements between chains decreases resulting in the increasing in distance between neighboring chains due to the material recovery to the equilibrium state. Furthermore, the average effective number of entanglements between chains participating in the deformation process is not the same between the loading (tension) and the unloading (retraction) because during loading all the chains are intermingling while during unloading, only chains that reached their limits are interacting inside the material.

Fig. 8. Simulated (dashed lines) and measured (continuous lines) cyclic stress-strain response of (a) HDPE, (b) LDPE and (c) ULDPE; \( E' = 4580 \text{ MPa}, \ E'' = 4.5 \text{ MPa}, \ \beta = 3.8, \ E'_\text{LDPE} = E''_\text{LDPE} = 1 \text{ MPa}, \ a_0 = \beta_0 = 0 \) (ULDPE/LDPE), \( a_0 = 1 \) (LDPE), \( \beta_0 = 0.38 \) (LDPE), \( a_1 = 5, \ \beta_1 = 18.13, \ c_1 = 40 \text{ MPa}, \ c_2 = 18 \text{ MPa} \) (ULDPE/LDPE), \( c_2 = 10 \text{ MPa} \) (HDPE), \( c_3 = 2.7 \text{ MPa}, \ c_0 = 386 \text{ s}, \ c_0 = 139 \text{ s}, \ c_4 = 5, \ c_3 = 3 \text{ MPa}^{-1}, \ D = 8.7 \times 10^{-8} \text{ MPa}^{-1}\text{s} \) (HDPE), \( D = 4 \times 10^{-6} \text{ MPa}^{-1}\text{s} \) (LDPE), \( D = 7 \times 10^{-6} \text{ MPa}^{-1}\text{s} \) (ULDPE), \( Q/R = 24.5 \times 10^2 \text{ K} \).
Therefore, an evolution of the density of chains accounted in the constitutive model is needed. During reloading and unloading, two different evolution equations are needed to capture the evolution of parameters.

The isotropic stress is a rate-independent contributor to the intermolecular stress. It is responsible for modeling strain-hardening or strain-softening in the material. During reloading, the orientation of the crystalline blocks and the amorphous linking along the loading direction leads to a substantial strain-hardening. Hence, the isotropic stress increases during reloading. During unloading, a part of the crystalline blocks and the amorphous linking loses orientation from the principal stretch direction, consequently the isotropic stress decreases. The drag stress is attributed to the difference between current yield strength and initial yield strength. In other words, it also controls the strain-hardening and strain-softening of the material. During loading, the drag stress increases with increasing strain since the material hardens at each cycle. During unloading, the material will return to its equilibrium state, chains will lose-up and lead to a decrease in the drag stress. As the strain increases during loading, the viscosity coefficient decreases. The interaction between neighboring chains decreases due to the stretching of the chains and increase in their individual velocities. The interaction between neighboring chains is constant at first. However, at large deformation after the specimen undergoes a few cycles, the chains interactions decrease due to breakage of chains, and the material deformation. This means that the specimen will try to resist deformation as much as possible as the strain increases. During unloading, a portion is recovered due to the recovery of the strain hence increasing the molecules interactions.

\begin{align*}
\text{Fig. 9. Normalized rubbery modulus kinetics under (a) loading } & C_r/C_{0r} = \left( \frac{\varepsilon}{\varepsilon_{\text{max}}} \right)^{0.5012} \text{ and (b) unloading } \\
& C_{rul}/C_{0r} = \left( \frac{\varepsilon_{\text{ul}}}{\varepsilon_{\text{max}}} \right)^{1.38} + 0.4963 \text{ for HDPE: } C_r = 0.45 \text{ MPa, } N_{0r} = 26, \text{ for LDPE: } \\
& C_r = 0.6 \text{ MPa, } N_{0r} = 120 \text{ and for ULDPE: } C_r = 0.70 \text{ MPa, } N_{0r} = 160.
\end{align*}

\begin{align*}
\text{Fig. 10. Normalized isotropic stress kinetics under (a) loading } & r_i/r_{0i} = 0.9788 \text{ and (b) unloading } \\
& r_{iul}/r_{0iul} = 1.576 \text{ for crystalline phase: } \\
& r_{i} = 22 \text{ MPa, } r_{0i} = 25 \text{ MPa and for amorphous phase: } \\
& r_{i} = 30 \text{ MPa, } r_{0i} = 32 \text{ MPa.}
\end{align*}
4. Concluding remarks

PE-based materials offer versatile mechanical properties, from stiff plastics to thermoplastic elastomers according to the crystal content, which confer them a wide range of potential applications for biomedical products design. The PE response is time-dependent, and when subjected to cyclic loading, in addition to hysteresis phenomena, its mechanical properties deteriorate. Therefore, understanding the deformation mechanisms involved during cyclic loading and development of predictive models for the mechanical behavior evolution are of prime importance for PE-based products design.

In this contribution, the Mullins effect is evidenced in PE with its crystal-dependency. A constitutive model is proposed based on the assumption that the PE macro-behavior is the consequence of two physically distinct sources acting in parallel, a viscoelastic-viscoplastic intermolecular resistance and a viscohyperelastic network resistance. Two different deformation mechanisms are supposed to take place due to the presence of the amorphous and crystalline phases in PE, and are integrated in the formulation of the constitutive model by means of a composite framework. The PE cyclic stretching features are captured by introducing evolution laws for the model parameters affected by the microstructure alteration due to the Mullins effect.

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