Mullins' effect in semicrystalline polymers

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Article info

Article history:
Received 3 March 2009
Received in revised form 1 May 2009
Available online 13 May 2009

Keywords:
Isotactic polypropylene
Viscoplasticity
Cyclic deformation
Mullins' effect
Constitutive equations

Abstract

Observations are reported on isotactic polypropylene in uniaxial cyclic tensile tests at room temperature. A model is derived for the viscoplastic response of semicrystalline polymers at three-dimensional deformations with small strains. Adjustable parameters in the stress–strain relations are found by fitting the experimental data. It is shown that polypropylene reveals some characteristic features of the Mullins effect that can be quantitatively predicted by the constitutive equations.

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1. Introduction

This paper is concerned with experimental investigation and constitutive modeling of cyclic viscoplasticity of isotactic polypropylene (iPP) with emphasis on the Mullins phenomena.

Observations in cyclic tensile tests on particle-reinforced rubbers reveal a number of phenomena that are conventionally referred to as Mullins’ effects (Mullins, 1947): (i) unloading and reloading paths of stress–strain diagrams differ substantially (hysteresis of energy), (ii) under cyclic deformation with a fixed maximum strain, stress monotonically decreases with number of cycles (strain-softening or damage accumulation), and (iii) when stretching proceeds after several cycles of loading–unloading and strain exceeds the maximum strain under cyclic deformation, the stress–strain curve rapidly reaches that for a virgin specimen (strain-hardening). For a detailed description of these features, see Diani et al. (2009).

As initial studies focused on the behavior of natural rubbers reinforced with carbon black (CB), Mullins’ phenomena were associated with mechanically induced transformations in the secondary network of CB particles (Mullins and Tobin, 1953; Bueche, 1961). Recent studies demonstrate that the above effects are revealed by a rather wide class of materials including elastomers reinforced with silica (Hanson et al., 2005; Suzuki et al., 2005; Botti et al., 2006) and magnetic particles (Coquelle and Bossis, 2006), ethylene–propylene–diene terpolymer (Cheng and Chen, 2003), thermoplastic elastomers (Qi and Boyce, 2005; Merabia et al., 2008; Drozdov, 2009), biological tissues (Franceschini et al., 2006; Ciarletta et al., 2008), double-network hydrogels (Webber et al., 2007), and fiber assemblies (Wilde et al., 2006).

It follows from this list that internal heterogeneity of polymers may be treated as a driving force for Mullins’ phenomena as homogeneous (unfilled) elastomers show a negligible difference between loading and unloading paths of their stress–strain diagrams (Meunier et al., 2008). This implies that semicrystalline polymers (where inhomogeneity is caused by crystalline lamellae distributed in a rubbery matrix) may demonstrate pronounced Mullins’ effects. The first aim of this study is to report experimental data on a conventional semicrystalline polymer that confirm this hypothesis.

Our observations show that not only loading paths of the stress–strain diagrams coincide for a virgin sample and a specimen subjected to cyclic deformation [see (iii) in the list of characteristic features of the Mullins effect], but their unloading paths are also identical (Fig. 6 below). In other words, a semicrystalline polymer looses entire memory about previous deformation provided that the current strain strongly exceeds the maximum strain under cyclic loading. As this property is in apparent contradiction with strain-softening (observed as a decrease in maximum stress and an increase in residual strain with number of cycles), the other objective of this study is to develop constitutive equations that reproduce quantitatively both strain-softening, strain-hardening, and fading memory.

Modeling of the Mullins effect in filled elastomers has been a focus of attention in the past decade (Ogden and Roxburgh, 1999; Miehe and Keck, 2000; Drozdov and Dorfmann, 2001; Dorfmann and Ogden, 2003, 2004; Chagnon et al., 2004, 2006; Horgan et al., 2004; Göktepe and Miehe, 2005; De Tommasi et al., 2006; Guo and Sluys, 2006; Meissner and Matejka, 2006; Kazakeviciute-Makovska, 2007; D’Ambrosio et al., 2008; Li et al., 2008; Harbour...
As it seems rather difficult to describe adequately the entire set of characteristic features of the mechanical response of rubbers under cyclic deformation, only one aspect of the Mullins phenomenon is conventionally taken into account.

Hysteresis of energy under cyclic loading is described within the concept of alteration (breakage and restoration) of links between polymer chains and between the matrix and inclusions (Chagnon et al., 2006; De Tommasi et al., 2006; D’Ambrosio et al., 2008). In a variant of this theory developed by Drozdov and Dorfmann (2001), detachment–attachment of chains is treated as their transition from flexed to extended conformation and vice versa. The latter is closely connected to the two-phase theory of composites (Johnson and Beatty, 1993).

To predict strain-softening of elastomers under cyclic deformation, their damage is taken into account (Govindjee and Simo, 1992). The simplest (pseudo-elastic) model treats a polymer as an elastic medium subjected to damage, whose accumulation is described by one internal variable (Ogden and Roxburgh, 1999; Dorfmann and Ogden, 2003, 2004; Horgan et al., 2004). Advanced models combining damage [either in the form of formation and growth of micro-defects or as a phenomenological measure of strain-softening (Chagnon et al., 2004)], viscoelasticity, and viscoplasticity were proposed by Gökştepe and Miehe (2005), Diani et al. (2006), Li et al. (2008), D’Ambrosio et al. (2008) and Aboudi (2009), to mention a few.

Unlike previous works that disregard strain-hardening or treat it only qualitatively, this study focuses on the quantitative description of the response of semicrystalline polymers when monotonic or non-monotonic stretching proceeds after cyclic loading. In the derivation of constitutive equations we confine ourselves to small deformations (this restriction is natural as necking of polyolefins occurs at tensile strains of about 20%) with a constant strain rate at ambient temperature. The Mullins effects are modeled within the viscoplasticity theory, which means that the viscoelastic response (observed in creep and relaxation tests) is disregarded.

To reduce the number of adjustable parameters in stress–strain relations, a semicrystalline polymer is treated as a homogeneous incompressible viscoplastic continuum. The incompressibility condition is introduced to simplify derivations only. It reflects the fact that polypropylene is a weakly compressible polymer, whose Poisson’s ratio $\nu$ ranges from 0.40 to 0.45 (Kolarik and Pegoretti, 2006). Although the medium is thought of as homogeneous, a difference between the responses of crystalline and amorphous phases is taken into account by assuming the plastic strain to be split into a sum of two parts. The strain rate for the first component is proportional to current stress (which means that this plastic strain monotonically grows under cyclic tensile deformation with a non-negative engineering stress), whereas the strain rate for the other component is proportional to that for macro-deformation (which implies that this plastic strain increases under stretching and decreases under retraction of a sample).

The exposition is organized as follows. Observations in uniaxial cyclic tensile tests are reported in Section 2, where characteristic features of Mullins’ effect in semicrystalline polymers are discussed. In Section 3, constitutive equations are derived by using the laws of thermodynamics. These stress–strain relations involve 5 adjustable parameters that are found by matching observations (one cycle of loading–unloading with a fixed maximum strain). It is demonstrated that the model adequately predicts the mechanical behavior in loading–unloading tests with other maximum strains as well. The governing equations cannot, however, correctly describe next cycles of loading–unloading as they neglect accumulation of damage on the one hand and fading of memory about history of deformation, on the other. An extension of the model that accounts for these phenomena is developed in Section 4. After determination of material constants in the generalized model, it is shown that the constitutive equations quantitatively predict stress–strain diagrams for cyclic tensile tests with arbitrary maximum strains and minimum stresses per cycle. Some concluding remarks are formulated in Section 5.

2. Experimental results

Isotactic polypropylene Novolen 1100 L (density 0.910 g/cm$^3$, melting temperature $T_m = 163 \degree C$, melt flow rate 8.0 g/10 min) was purchased from Targor GmbH (Germany). Dumbbell specimens (ASTM standard D638) with the cross-sectional area 9.95 $\times$ 3.84 mm were molded by using an injection-molding machine Ferromatic K110/S60-2K.

Mechanical tests were performed at room temperature with the help of a universal testing machine Instron-5568 equipped with electro-mechanical sensors for the control of longitudinal strains in the active zone of samples. The tensile force was measured by a standard load cell. The engineering stress $\sigma$ was determined as the ratio of axial force to cross-sectional area of specimens in the stress-free state.

The experimental program involved 4 series of tests. Each test was conducted on a new sample. All tests were repeated 3 times to confirm good repeatability of observations.

First, stretching of a sample was performed with a cross-head speed 10 mm/min (the strain rate $\dot{\epsilon} = 2 \times 10^{-3}$ s$^{-1}$) up to its fracture. Observations are reported in Fig. 1, where $\sigma$ is plotted versus tensile strain $\epsilon$. This figure shows that the stress–strain diagram under tension is strongly nonlinear. Yielding occurs at a strain $\epsilon_y \approx 0.11$, and necking begins at a strain $\epsilon_n \approx 0.19$.

All other tests were carried out with the same strain rate $\dot{\epsilon} = 2 \times 10^{-3}$ s$^{-1}$ for two reasons: (i) it provided a relatively wide interval of strains for investigation (when $\epsilon$ was increased by an order of magnitude, the necking strain was reduced to 0.14), and (ii) it ensured that the deformation program was performed rather accurately (discrepancies in maximum strains per cycle did not exceed 0.002). A shortcoming of this choice is that viscoelastic effects (disregarded in constitutive modeling) cannot be entirely excluded from consideration (the maximum duration of tests was about 5 min, whereas tensile relaxation tests show a reduction in stress during this period of about 20%).

The second series consisted of 3 loading–unloading tests (2 cycles) with maximum strains $\epsilon_{\max} = 0.049, 0.098$, and 0.152 and a determination of material constants in the generalized model, it is shown that the constitutive equations quantitatively predict stress–strain diagrams for cyclic tensile tests with arbitrary maximum strains and minimum stresses per cycle. Some concluding remarks are formulated in Section 5.

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minimum stress \( \sigma_{\text{min}} = 0.2 \) MPa (a non-zero minimum stress was chosen to avoid buckling of specimens). In a test, a sample was stretched up to the maximum strain \( \varepsilon_{\text{max}} \), unloaded down to the minimum stress \( \sigma_{\text{min}} \), reloaded up to the strain \( \varepsilon_{\text{max}} \), and unloaded down to the zero stress. Experimental data are depicted in Fig. 2 which shows that

1. The stress–strain diagrams at loading and retraction are strongly nonlinear.
2. Shapes of the loading and reloading paths differ substantially, whereas retraction paths for the first and subsequent unloading are similar.
3. The hysteresis energy (estimated as the area between unloading and subsequent reloading curves) noticeably increases with \( \varepsilon_{\text{max}} \).
4. Maximum stresses per cycle decrease, while residual strains (at which tensile stress vanishes at unloading) increase with number of cycles.

The third series involves two cyclic tests with growing (from cycle to cycle) maximum strain and various minimum stresses \( \sigma_{\text{min}} \). In the first test, maximum strains read \( \varepsilon_{\text{max}} = 0.034, \varepsilon_{\text{max}} = 0.083, \varepsilon_{\text{max}} = 0.133, \varepsilon_{\text{max}} = 0.186 \), and the minimum stress \( \sigma_{\text{min}} = 0.05 \) MPa. In the other test, maximum strains are \( \varepsilon_{\text{max}} = 0.030, \varepsilon_{\text{max}} = 0.059, \varepsilon_{\text{max}} = 0.091, \varepsilon_{\text{max}} = 0.123, \varepsilon_{\text{max}} = 0.154, \varepsilon_{\text{max}} = 0.184 \), and \( \sigma_{\text{min}} = 2.4 \) MPa. Observations are presented in Figs. 3 and 4 together with results of numerical simulation for loading–unloading tests (1 cycle) with appropriate maximum strains. The following conclusions are drawn from the experimental data:

1. When stretching proceeds after a cycle of loading–unloading, the stress–strain curve rapidly reaches that for a virgin (not subjected to cyclic deformation) specimen, in accord with conventional observations on Mullins’ effect in particle-reinforced elastomers.
2. Unloading paths of the stress–strain diagrams of specimens subjected to cyclic pre-loading (circles) coincide with those of samples not suffered cyclic deformation (solid lines).
3. The above results are independent of whether retraction under cyclic deformation is performed down to the zero stress (Fig. 3) or to some positive stress (Fig. 4).

The last series of tests was performed to reveal some peculiarities of the Mullins effect in isotactic polypropylene. To show that the coincidence of loading paths of stress–strain diagrams for virgin and cyclically pre-loaded specimens (when tensile strain exceeds the maximum strain per cycle) is weakly affected by number of cycles under cyclic deformation, three additional tests were conducted. In these tests, specimens were subjected to cyclic deformation (5 cycles of loading–unloading with maximum strains \( \varepsilon_{\text{max}} = 0.048, 0.10, \) and \( 0.148 \) and the minimum stress \( \sigma_{\text{min}} = 0.8 \) MPa). After this procedure, stretching of samples proceeded until their necking. Experimental data are reported in Fig. 5 (symbols) together with results of numerical simulation for loading–unloading of virgin specimens. This figure clearly demonstrates Mullins’ effect and shows that even severe (5 cycles) pre-loading does not influence the stress–strain diagrams when tensile strain exceeds maximum strains per cycle.
To validate that unloading curves coincide for virgin and pre-loaded samples, two tests were carried out. In the first, a sample was subjected to 2 cycles of deformation with maximum strains $\varepsilon_{\text{max}} = 0.049$ and 0.1 and the zero minimum stress, whereas in the other test, a specimen suffered only one cycle of loading–unloading with the maximum strain $\varepsilon_{\text{max}} = 0.1$. Observations depicted in Fig. 6 show excellent agreement between unloading paths of the stress–strain curves.

### 3. Constitutive model

Our aim now is to derive constitutive equations in viscoplasticity of semicrystalline polymers that correctly describe the first cycle of deformation. An extension of this model that accounts for inelastic deformations in amorphous and crystalline phases, respectively. The difference between these tensors is that the rate-of-strain tensor $\dot{\varepsilon}$ of-strain tensor for macro-deformation $\varepsilon$ is neglected. The inequality $U < 0$ means that the directions of

$$Q = \frac{\text{d}W}{\text{d}t} + \dot{\sigma} : \dot{\varepsilon} > 0,$$

where $Q$ stands for internal dissipation per unit volume and unit time, we find that the second law of thermodynamics is satisfied, provided that the stress tensor is given by

$$\dot{\sigma} = -p \dot{I} + \mu (1 - \phi) \dot{\varepsilon},$$

where $p$ stands for an unknown pressure, and $\dot{I}$ is the unit tensor. It follows from Eqs. (4) and (5) that the rate of internal dissipation is proportional to strain energy,

$$A \dot{\phi} = A(\Phi + \kappa \varepsilon_{\text{p}}^3 - \Phi)^2,$$

where $A, \kappa > 0$ and $\Phi \in (0, 1)$ are adjustable parameters, and $\varepsilon_{\text{p}}^3 = \frac{1}{2} (\varepsilon_{\text{p}} : \varepsilon_{\text{p}})$ stands for an equivalent plastic strain in crystallites. Eq. (6) with the zero initial condition implies that $\phi$ vanishes in the reference state, monotonically increases with time, and approaches its ultimate value at relatively large deformations [this value equals $\Phi$ when the second term in the right-hand side of Eq. (6) is neglected]. The inequality $\Phi < 1$ means that the directions of plastic flow and macro-deformation coincide.
Eq. (6) with $\kappa = 0$ resembles a kinetic equation for a chemical reaction of the second order. Although some justification of this order may be provided (plastic flow in the amorphous phase induces slippage of crystallites, which, in turn, accelerates inelastic deformation in the matrix), this relation is treated as phenomenological. The term $\kappa \varepsilon_i^{(p)}$ is introduced to account for the effect of changes in morphology of crystallites on the plastic strain rate in the amorphous phase.

Eqs. (1)–(3), (5), and (6) provide stress–strain relations for an arbitrary three-dimensional deformation at small strains. An advantage of the model is that the constitutive equations (i) preserve the same form for loading and retraction, (ii) do not take into account the strain $\varepsilon_{\text{max}}$ at which retraction starts (which implies that they can be easily verified), and (iii) involve only 5 material constants ($\mu, A, B, \Phi$, and $\kappa$).

### 3.2. Uniaxial tension

We now consider uniaxial tension of an incompressible specimen. Bearing in mind that the strain tensors $\varepsilon_i, \varepsilon_r, \varepsilon_{p1}$, and $\varepsilon_{p2}$ are entirely characterized by appropriate scalar functions $\varepsilon_i, \varepsilon_r, \varepsilon_{p1}$, and $\varepsilon_{p2}$, respectively, we find from Eqs. (1) and (2) that

$$\varepsilon_r = \varepsilon - \varepsilon_{p1} - \varepsilon_{p2}.$$  

Inserting this expression into Eq. (5) and taking into account boundary conditions in stresses at the lateral surface of the sample, we calculate the tensile stress

$$\sigma = E[(1 - v)(\varepsilon - \varepsilon_{p1} - \varepsilon_{p2})],$$  

where $E = \frac{1}{2} \mu$ denotes the Young’s modulus [the latter formula follows from the general expression for Young’s modulus of a compressible viscoplastic medium $E = \mu/(1 + v)$ when Poisson’s ratio approaches its limiting value $v = 0.5$; the account for compressibility of polypropylene with $v = 0.4$ (Kolarik and Pegoretti, 2006) results in an increase in $E$ by approximately 7%].

It follows from Eqs. (3) and (6) that the functions $\varepsilon_{p1}, \varepsilon_{p2}$ and $\phi$ are governed by the differential equations

$$\frac{d\varepsilon_{p1}}{d\varepsilon} = \phi, \quad \frac{d\varepsilon_{p2}}{d\varepsilon} = \pm \frac{b}{E} \sigma, \quad \frac{d\phi}{d\varepsilon} = \pm a (\Phi + \kappa \varepsilon_{p2} - \phi)^2,$$

where $a = A/|\varepsilon|, b = B/|\varepsilon|$, and the signs $+$ and $-$ correspond to loading and unloading, respectively.

### 3.3. Material constants

Adjustable parameters in Eqs. (7) and (8) are found by fitting observations at loading–unloading with $\varepsilon_{\text{max}} = 0.152$ (Fig. 2) by using the following algorithm. We fix some intervals $[0, a_i], [0, b_i], [0, \Phi_i]$, and $[0, \kappa_i]$, where the best-fit parameters $a, b, \Phi$, and $\kappa$ are assumed to be located, and divide these intervals into $J = 10$ sub-intervals by the points $a^{(0)} = \Delta a, b^{(0)} = \Delta b, \Phi^{(0)} = \Delta \Phi, \kappa^{(0)} = \Delta \kappa$ with $\Delta a = a_i/\Delta \varepsilon, \Delta b = b_i/\Delta \varepsilon, \Delta \Phi = \Phi_i/\Delta \varepsilon, \Delta \kappa = \kappa_i/\Delta \varepsilon, i = 0, 1, \ldots, J - 1$. For each set $\{a^{(0)}, b^{(0)}, \Phi^{(0)}, \kappa^{(0)}\}$, the functions $\varepsilon_{p1}, \varepsilon_{p2}$, and $\phi$ are determined by numerical integration of Eq. (8) with the zero initial conditions. Integration is performed by Runge–Kutta method with the step $|\Delta \varepsilon| = 1.0 \times 10^{-5}$. The Young’s modulus $E$ is found by the least-squares technique from the condition of minimum of the function

$$F = \sum_m \left[ \sigma_{\text{exp}}(\varepsilon_m) - \sigma_{\text{num}}(\varepsilon_m) \right]^2,$$

where summation is performed over all strains $\varepsilon_m$ at which observations are reported, $\sigma_{\text{exp}}$ is the stress measured in the test, and $\sigma_{\text{num}}$ is given by Eq. (7). The quantities $a, b, \Phi$, and $\kappa$ are determined from the condition of minimum of function (9). Afterwards, the initial intervals are replaced with the new intervals $[a - \Delta a, b + \Delta b, \Phi - \Delta \Phi, \kappa - \Delta \kappa, \kappa + \Delta \kappa]$, and the calculations are repeated. The best-fit constants $a, b, \Phi$, and $\kappa$ are collected in Table 1.

### 3.4. Validation of the model

To examine ability of the constitutive equations to predict the mechanical response of IPP, we, first, perform numerical simulation of the stress–strain diagram at stretching up to the necking point. Fig. 1 demonstrates good agreement between the experimental data and the results of numerical analysis at all strains $\varepsilon$ below $\varepsilon_{\text{max}}$.

Afterwards, simulation is performed of stress–strain curves in cyclic tests with $\varepsilon_{\text{max}} = 0.049$ and 0.098. Figs. 2 and 6 reveal excellent agreement between the observations in appropriate tests at retraction and predictions of the model.

Finally, simulation is carried out of loading–unloading curves with the maximum strains at which retraction starts in cyclic tests whose results are reported in Figs. 3 and 4. Comparison of the observations with the results of numerical analysis confirms that the model adequately predicts the experimental data in cyclic tests with all maximum strains under consideration.

### 4. Extension of the constitutive equations

Although the model derived in Section 3 correctly describes experimental data in one-cycle tests, it cannot be employed for the analysis of tensile tests with several cycles. This may be explained by the observation that reloading paths of the stress–strain curves depicted in Figs. 2–4 distinguish noticeably from the loading path at stretching of a virgin sample. Within the concept of pseudo-elasticity (Ogden and Roxburgh, 1999), this difference is accounted for by adopting a new expression for the strain energy density of a pre-loaded medium, whose connections with the “old” elastic energy are established through some damage parameter. A shortcoming of that approach is that it cannot adequately describe evolution of residual strains under cyclic loading. Generalized models in pseudo-elasticity that capture growth of residual strains (e.g., Dorfmann and Ogden, 2004) lead, however, to overly complicated stress–strain relations whose predictive power is limited due to the presence of several adjustable functions.

Our aim now is to develop constitutive equations that capture the difference between loading and reloading curves on the one hand and can be applied to predict observations, on the other. For brevity, we confine ourselves to the analysis of second cycles of loading–retraction only, but presume that unloadings and reloadings start at arbitrary stresses and strains.

As this study focuses on cyclic deformations with small strains, quadratic expression (4) for the strain energy density cannot be revisited, while appropriate changes are made in evolution Eq. (6). With reference to the pseudo-elasticity theory (grounded on a hypothesis that a particle-reinforced elastomer looses memory about its mechanical properties in the virgin state after a cycle of deformation), we postulate that memory of a semicrystalline polymer about history of plastic flow in the amorphous phase rapidly decays upon reloading. Keeping in mind that the coefficient $\phi$ in

<table>
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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>$E$ (GPa)</td>
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</tr>
<tr>
<td>$a$</td>
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</tr>
<tr>
<td>$b$</td>
<td>19.8</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>0.67</td>
</tr>
<tr>
<td>$\kappa$</td>
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</table>
Eq. (5) is a continuous function of time, we write for the second cycle of loading–unloading,

$$\phi = \phi_1 + \phi_2,$$  \hspace{1cm} (10)

where $\phi_1$ is a decreasing function of time (preserving information about previous deformations), and $\phi_2$ characterizes plastic strain rate in the amorphous phase driven by current strains. The decrease in $\phi_1$ with time is governed by the phenomenological equation

$$\frac{d\phi_1}{dt} = -\gamma \left( \frac{\phi_{1(t)}}{\phi_{1}} \right)^q, \quad \phi_{1(t)} = \phi_{1},$$ \hspace{1cm} (11)

where $\gamma$ and $q$ are positive parameters, and $\phi_{1(t)}$ is the value of $\phi$ at the instant $t_1$ when starts. Evolution of the function $\phi_2$ is described by the differential equation similar to Eq. (6).

$$\frac{d\phi_2}{dt} = A_2(\Phi + Kc^{eq}_{p2} - \phi_2)^2, \quad \phi_2(t_1) = 0.$$ \hspace{1cm} (12)

To reduce the number of adjustable parameters, we suppose that only the ratio $A_2$ at reloading differs from that at first loading $A$, while the other coefficients (the ultimate rate of plastic flow in the amorphous matrix $\Phi$ and the parameter $K$ that characterizes the influence of plastic deformation of crystallites on the rate of sliding of junctions in the amorphous phase) remain unchanged. This assumption is equivalent to the hypothesis that plastic flow in the amorphous matrix at relatively large deformations is not affected by transformations of the crystalline structure under the first loading and reloading. It is confirmed by our numerical analysis of reloading paths (not presented) which shows that treatment of all coefficients ($A$, $\Phi$, and $K$) in Eq. (6) as adjustable parameters does not improve the quality of fitting noticeably.

For simplicity, it is presumed that Eq. (3) for plastic flow in the crystalline phase preserves its form at reloading. This implies that each reloading curve is determined by three material constants, $\gamma$, $q$, and $K = A_2/A$. Fitting of experimental data ensures rather high accuracy in determination of these parameters because not only appropriate reloading paths in cyclic tests, but the loading path for stretching of a virgin sample at $\epsilon > \epsilon_{max}$ are taken into account in the approximation (due to the Mullins effect). To enhance stability of the fitting algorithm, we suppose that the exponent $q$ remains the same for all reloading curves, which implies that each stress–strain diagram is characterized by two parameters, $\gamma$ and $K$, only.

Simultaneous approximation of all stress–strain curves for the second cycle of deformation with only 2 adjustable parameters seems rather difficult. Hence, we presume the rate of plastic strain in the crystalline phase $d\varepsilon_{p2}/dt$ to be affected by previous cyclic deformation. To reduce the number of material constants, it is postulated that Eq. (3) is valid under both reloading and second unloading. Under reloading, we use the same coefficient $B$ that was determined in the approximation of the first cycle of deformation. Under the second unloading, Eq. (3) reads

$$\frac{d\varepsilon_{p2}}{dt} = (1 - T)B\sigma^\gamma,$$ \hspace{1cm} (13)

where $T \in [0, 1]$ is a coefficient that accounts for “memory” of crystallites about history of cyclic deformation: $T$ adopts some positive value $L$ when the second unloading starts at the same maximum strain $\epsilon_{max}$ as the first cycle of deformation, it monotonically decreases with $\epsilon_{max}$, and vanishes at $\epsilon_{max} > \epsilon_{max}$ (when the material loses entire memory about previous deformations). The fading memory effect is described by the quasi-Gaussian dependence

$$T = L \exp\left[ -\frac{1}{\epsilon^2} (\varepsilon_{p2}^{(1)} - \varepsilon_{p2}^{(2)}) : (\varepsilon_{p2}^{(1)} - \varepsilon_{p2}^{(2)}) \right],$$ \hspace{1cm} (14)

where $\varepsilon_{p2}^{(1)}$ and $\varepsilon_{p2}^{(2)}$ stand for plastic strain tensors in the crystalline phase at the instants $t^{(1)}$ and $t^{(2)}$ when unloading starts for the first and second time, respectively, and the strain $\varepsilon$ characterizes memory about history of deformations.

For each maximum strain tensor $\varepsilon_{max}^{eq}$ at the first cycle of deformation, the viscoplastic behavior of a semicrystalline polymer at the second cycle of loading–unloading is determined by Eqs. (1)–(3), (5) and (10)–(13) with 3 adjustable parameters $\gamma$, $K$, and $L$. To establish correlations between these quantities and internal variables in the model, the following equations are adopted:

$$\log \gamma = \gamma_0 - \gamma \varepsilon_{p2}^{eq}, \quad K = K_0 - K_1 \phi_{1}, \quad L = L_0 \Delta \varepsilon_{p2}^{eq},$$ \hspace{1cm} (15)

where $\gamma_0$, $K_0$ ($m = 0, 1$) and $L_0$ are constants, $\log = \log_{10}$, $\varepsilon_{p2}^{eq} = (\varepsilon_{p2}^{(1)} : \varepsilon_{p2}^{(1)})$ is the equivalent plastic strain at the instant $t_1$ when reloading starts, $\Delta \varepsilon_{p2}^{eq} = (\varepsilon_{p2}^{eq} : \varepsilon_{p2}^{eq})$ denotes the equivalent increment of plastic strains in crystallites, and $\Delta \varepsilon_{p2} = \varepsilon_{p2}^{(1)} - \varepsilon_{p2}^{(2)}$.

### 4.1. Uniaxial tension

Under uniaxial tension, the engineering stress $\sigma$ is given by Eq. (7) with $\varepsilon_{p1}$ obeying Eq. (8) and $\varepsilon_{p2}$ satisfying the equations

$$\frac{d\varepsilon_{p2}}{d\varepsilon} = \frac{b}{E} \sigma, \quad \frac{d\varepsilon_{p2}}{d\varepsilon} = \frac{b}{E} (1 - I) \sigma.$$ \hspace{1cm} (16)

The function $\phi$ is determined by Eq. (10), where $\phi_1$ and $\phi_2$ are governed by

$$\frac{d\phi_1}{d\varepsilon} = \pm \Gamma \left( \frac{\phi_{1(t)}}{\phi_{1}} \right)^q, \quad \frac{d\phi_2}{d\varepsilon} = \pm K(\Phi + Kc_{p2} - \phi_2)^2$$ \hspace{1cm} (17)

with $\Gamma = \gamma/|\varepsilon|$. The signs $+$ and $-$ in Eqs. (16) and (17) correspond to reloading and unloading, respectively. Phenomenological relations (15) read

$$\log \Gamma = \Gamma_0 - \Gamma_1 \varepsilon_{p2}^{eq}, \quad K = K_0 - K_1 \phi_{1}, \quad L = L_0 \Delta \varepsilon_{p2},$$ \hspace{1cm} (18)

where $\Delta \varepsilon_{p2} = \varepsilon_{p2}^{(1)} - \varepsilon_{p2}^{eq}$ and $\varepsilon_{p2}^{eq}$ denote total plastic strain and plastic strain in the crystalline phase at the instant $t_1$ when first reloading starts, while $\varepsilon_{p2}^{(1)}$ stands for plastic strain in crystallites at the instant $t_1$ when first unloading starts. Eq. (14) is presented in the form

$$L = \exp \left( -\frac{\delta \varepsilon_{p2}}{\epsilon} \right),$$ \hspace{1cm} (19)

where $\delta \varepsilon_{p2} = \varepsilon_{p2}^{(2)} - \varepsilon_{p2}^{(1)}$ and $\varepsilon_{p2}^{(1)}$ and $\varepsilon_{p2}^{(2)}$ are plastic strains in crystallites at the instants $t^{(1)}$, $t^{(2)}$ when the first and second unloading.

### 4.2. Material constants

To determine adjustable parameters $I_0$, $I_1$, $K_0$, $K_1$, $L$, and $\epsilon$ that characterize the viscoplastic response at the second cycle of loading–unloading, the following algorithm is applied.

We begin with matching the experimental data at reloading for the cyclic test with $\varepsilon_{max} = 0.152$ (at $\epsilon < \varepsilon_{max}$, Fig. 2) together with the observations at uniaxial tension (at $\epsilon > \varepsilon_{max}$, Fig. 1) by using the quantities $E$, $a$, $b$, $\phi$, and $K$ listed in Table 1. First, Eqs. (7) and (8) are integrated numerically from $\epsilon = 0$ to $\epsilon = \varepsilon_{max}$, and from $\epsilon = \varepsilon_{max}$ to $\sigma = \sigma_{min}$. Then, some intervals $[0, I^{(0)}]$, $[0, q]$, and [0, $K^{(0)}$] are fixed where the best-fit parameters $I$, $q$, and $K$ are located. These intervals are divided into $J = 10$ sub-intervals by the points $I^{(0)} = I^{(0)}; q^{(0)} = q^{(0)}; K^{(0)} = K^{(0)}$ with $\Delta I = I^{(0)} - I^{(0)}$, $\Delta q = q^{(0)} - q^{(0)}$, $\Delta K = K^{(0)} - K^{(0)}$. For each triplet $(I^{(0)}, q^{(0)}, K^{(0)})$, Eqs. (16) and (17) are integrated from $\sigma = \sigma_{min}$ to $\epsilon = \varepsilon_{max}$. The stress $\sigma$ is calculated from Eq. (7). The quantities $I$, $q$, and $K$ are found from the condition of minimum of function (9). Afterwards, the
The data are approximated by Eq. (19), where the coefficients are determined by the least-squares method. This coefficient is reported in Table 2.

We proceed with fitting the observations at second retraction reported in Fig. 2. Each set of experimental data is approximated separately by means of the above algorithm with the only parameter \( \Gamma = L \). The best-fit values of \( L \) are plotted versus \( \Delta \epsilon_{p2} \) in Fig. 9. The data are matched by Eq. (18), where the coefficient \( L_0 \) is determined by the least-squares method. This coefficient is reported in Table 2.

To assess the characteristic strain \( \epsilon \), we, first, calculate the parameter \( \Gamma \) for cyclic tests where the first unloading starts at \( \epsilon_{max1} = 0.049 \) and 0.098, and the second begins at \( \epsilon_{max2} = 0.098 \) and 0.152 (Fig. 10). To enlarge the amount of “experimental data”, we consider also hypothetical tests (Fig. 11), where the first retraction starts at \( \epsilon_{max1} = 0.049 \), 0.098, and 0.152, and the second starts at \( \epsilon_{max2} = 0.3 \) (it is assumed that the difference \( \epsilon_{max2} - \epsilon_{max1} \) is sufficiently large for \( \epsilon_{max1} = 0.049 \) to set \( \Gamma = 0 \) in approximation of the second unloading). The best-fit values of \( L \) calculated from the condition of minimum of function (9) are plotted versus \( \Delta \epsilon_{p2} \) in Fig. 12. The data are approximated by Eq. (19), where \( \epsilon \) is determined by the method on nonlinear regression. This constant is given in Table 2.

To evaluate quality of fitting, numerical simulation is conducted of the stress–strain relations with the material constants listed in Tables 1 and 2 for cyclic tests whose results are depicted in Figs. 2, 6, 10, and 11. These figures demonstrate that the constitutive model correctly describes the observations.

4.3. Validation of the model

To examine ability of the model to predict the viscoplastic response, an additional cyclic test is performed with \( \epsilon_{max1} = 0.032 \), \( \epsilon_{max2} = 0.083 \) and \( \sigma_{min} = 0.4 \) MPa. The observations are plotted in Fig. 13 together with the results of numerical simulation. This figure reveals good agreement between the experimental data and predictions of the model.

To demonstrate that the constitutive equations adequately predict the mechanical behavior in cyclic tests with nonzero minimum stresses, two tests are conducted with \( \epsilon_{max1} = 0.05 \), \( \epsilon_{max2} = 0.1 \) and minimum stresses \( \sigma_{min1} = 2 \) and 5 MPa. Fig. 14 shows that the results of numerical analysis are in accord with the experimental data in these experiments.

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**Table 2**

Adjustable parameters in Eqs. (16)–(19).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q )</td>
<td>4.2</td>
</tr>
<tr>
<td>( I_0 )</td>
<td>3.05</td>
</tr>
<tr>
<td>( F_1 )</td>
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</tr>
<tr>
<td>( K_0 )</td>
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</tr>
<tr>
<td>( K_1 )</td>
<td>1.51</td>
</tr>
<tr>
<td>( L_0 )</td>
<td>38.89</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>2.73 \times 10^{-2}</td>
</tr>
</tbody>
</table>
To assess how the Mullins phenomena are affected by $\epsilon_{\text{max}}$, numerical simulation is carried out of the stress–strain relations for cyclic tests with relatively small (0.03) and large (0.08) maximum strains in the first cycle. The results depicted in Fig. 15 reveal that the model correctly reproduces Mullins’ effect (coincidence of the loading path for a virgin sample with the reloading path for a specimen subjected to cyclic pre-loading) when tensile strain $\epsilon$ exceeds $\epsilon_{\text{max}}$ by approximately 0.03, and this increment is independent of $\epsilon_{\text{max}}$.

To show that the governing equations reproduce the second retraction path independently of where the first retraction starts and at which minimum stress reloading begins, numerical simulation is conducted of cyclic tests with $\epsilon_{\text{max}}=0.06$, $\epsilon_{\text{max}}=0.152$, $\sigma_{\text{min}}=4$ MPa, and $\epsilon_{\text{max}}=0.06$, $\epsilon_{\text{max}}=0.083$, $\sigma_{\text{min}}=4$ MPa. The results are compared in Fig. 16 with the experimental data in one-cycle test with $\epsilon_{\text{max}}=0.152$. This figure confirms that the constitutive model correctly predicts the stress–strain diagrams at unloading.

5. Concluding remarks

Observations have been reported in uniaxial cyclic tensile tests on isotactic polypropylene Novolen 1100 L at ambient temperature. The experimental data reveal characteristic features of the Mullins effect:

1. Strain-softening under cyclic deformation with a fixed maximum strain (a decrease in the maximum stress and an increase in residual strain with number of cycles).
2. Strain-hardening when stretching proceeds after cyclic deformation (coincidence of loading paths for a virgin sample with that for a specimen subjected to cyclic pre-loading).
3. Rapid fading of memory about deformation history (coincidence of retraction paths for samples subjected to different cyclic programs when the current strain exceeds maximum strains in previous cycles).
Constitutive equations are developed in cyclic viscoplasticity of semicrystalline polymers. Adjustable parameters in the stress–strain relations are found by fitting the experimental data. Although the number of material constants is relatively high, the model demonstrates the following advantages: (i) not more than 4 parameters are determined in approximation of each path (loading and unloading) of stress–strain diagrams, (ii) the governing equations quantitatively predict observations in cyclic tests, and (iii) both strain-softening and strain-hardening are correctly captured by the constitutive equations. The following shortcomings are to be mentioned: (i) kinetic equations for evolution of internal variables are merely phenomenological, (ii) the stress–strain relations have been verified for uniaxial tension only, which implies that their application to the analysis of three-dimensional deformations should be treated with caution (in particular, they disregard anisotropy of the Mullins effect [Göktepe and Miehe, 2005; Diani et al., 2006; Itskov et al., 2006]), and (iii) the model treats viscoelastic effects in a simplified manner (as a growth of plastic strain in crystallites with stress), which may result in deviations of predictions from observations in tests where intervals of cyclic loading are interrupted by relatively long intervals of creep or relaxation.

The simplified constitutive model derived in Section 3 appears to be optimal to predict the mechanical behavior of semicrystalline polymers under loading–unloading. The stress–strain relations involving 5 material constants correctly predict observations in cyclic tests with arbitrary maximum strains per cycle. The extension of this model developed in Section 4 adequately reproduces the response of semicrystalline polymers under the second cycle of loading–unloading. It also provides a way to generalize the governing equations for subsequent cycles of deformation [by splitting the function \( \phi \) into the sum of an “old” decreasing component and a “new” growing component by analogy with Eq. (10)]. An advantage of our approach is that the constitutive model correctly predicts the mechanical behavior of polypropylene under cyclic loading with arbitrary maximum stresses and minimum stresses (to the best of our knowledge, previous models fail to reproduce it quantitatively). Its drawbacks are (i) a noticeable growth in the number of adjustable parameters (Table 2 with 7 constants), and (ii) asymmetry in treatment of evolution of plastic strain in crystallites (the coefficient \( b \) is preserved at reloading and is modified at the second retraction).

Although changes in the rate of plastic flow due to (i) accumulation of damage and (ii) healing of micro-defects in polymers seem natural [Plaisted and Nemat-Nasser, 2007], the physics of these processes is not entirely understood. As a result, Eqs. (13) and (14) are taken for convenience of determination of material constants only. A similar remark can be done regarding phenomenological Eq. (18), where internal variables are chosen to ensure the best fit of data for \( \Gamma \), \( K \), and \( L \).

The present paper focuses on cyclic deformation of polypropylene with a fixed strain rate at room temperature. Analysis of the effects of strain rate and temperature on Mullins’ phenomena in semicrystalline polymers will be the subject of a subsequent work.

**Acknowledgement**

This study is partially supported by the European Commission through project Nanotough 213436.
References


