An experimental, theoretical and numerical investigation of shape memory polymers

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1. Introduction

Shape memory materials represent an important class of smart materials with the ability to return from a deformed state to the original shape. Such a property, known as shape memory recovery, is generally induced by an external stimulus such as heat, electricity or magnetism and allows the exploitation of shape memory materials in a wide range of applications (Wei et al., 1998a,b).

Among the others, shape memory polymers (SMPs) possess the advantages of large elastic deformations, low energy consumption for shape programming, low cost and density, potential biocompatibility, biodegradability, and excellent manufacturability (Hu et al., 2012; Feninat et al., 2002). As an example, SMPs can recover an elongation as large as 150%, which is significantly larger than the largest shape recovery observed in shape memory alloys, which is about 8% (Lendlein and Kelch, 2002). Moreover, SMPs are less expensive than shape memory alloys and they need a cheaper process for the production of different shapes and sizing.

Thanks to such characteristics, SMPs are very interesting for their potential innovative applications as, e.g., MEMS devices, actuators, temperature sensors, packaging, fibers and films with insulating properties, biomedical devices, and damping elements (Monkman, 2000; Sai, 2010; Tey et al., 2001; Poilane et al., 2000).
The mechanism responsible for shape memory in polymers is not related to a single material property of a specific polymer; rather, it results from the combination of polymer structure and morphology, together with the applied processing and heat treatment. In fact, shape memory behavior can be observed for several polymers that may differ significantly in their chemical composition.

Despite the increasing interests, only a few SMPs are described in the literature. As an example, various studies are devoted to polymers based on polyurethanes (Kim et al., 1996, 1998; Yang et al., 2006), ethylene/vinyl acetate copolymers, poly(ε-caprolactone), and semi-crystalline polymers and related blends (Zhu et al., 2003, 2005, 2006; Pandini et al., 2012).

Several experimental investigations have been conducted to characterize SMP behavior (Tobushi et al., 1997, 1998; Lendlein and Kelch, 2002; Abrahamson et al., 2003; Gall et al., 2002; Liu et al., 2004, 2006; Baer et al., 2007; Atlı et al., 2009; Kolesov et al., 2009; Kim et al., 2010; Volk et al., 2010a,b). Initial studies have mainly focused on material response under small deformations, i.e., under extensions less than 10% (Liu et al., 2006; Tobushi et al., 1998, 1997); recently, experimental campaigns have investigated the response under finite deformations, i.e., under extensions greater than 10% (Atlı et al., 2009; Voit et al., 2010a,b; Volk et al., 2010a,b; Wilson et al., 2007; Baer et al., 2007).

In addition to experimental investigations, the ever increasing number of SMP-based applications has motivated a considerable part of the research on the prediction and description of material behavior, through the development of appropriate and reliable constitutive models. However, such research field is still under progress, due to the complex behavior of SMPs. As already pointed out, there is a lack of modeling of shape memory effect in polymers, in spite of the fact that polymers represent a good and promising alternative to, e.g., shape memory alloys which have been widely studied from the point of view of both theoretical and numerical aspects (Lagoudas et al., 2012; Lexcellent et al., 2000; Sedláček et al., 2012).

Several macroscopic or phenomenological constitutive models (Liu et al., 2006; Chen and Lagoudas, 2008a,b; Qi et al., 2008; Kim et al., 2010; Reese et al., 2010; Xu and Li, 2010; Baghani et al., 2012) as well as microscopic or physical-based models (Barot et al., 2008; Nguyen et al., 2008; Srivastava et al., 2010) have been proposed to describe SMP behavior in both the small and finite deformation regimes. In the following, we focus on macroscopic modeling approaches which appear to be a powerful tool for the direct simulation of SMP applications, thanks to their simple numerical implementation and reduced time-consuming calculations, compared to microscopic approaches.

Most of the earlier modeling research has introduced rheological models consisting of spring, dashpot, and frictional elements in one-dimensional models, in order to quantitatively describe the shrinkage behavior in amorphous polymers (Khanakdar et al., 2007; Pakula and Trznadel, 1985; Trznadel and Kryszewski, 1988; Tobushi et al., 1997, 2001; Bhattacharyya and Tobushi, 2000; Abrahamson et al., 2003). However, despite their simplicity, such models usually lead to predictions agreeing only qualitatively with experiments.

Approaches involving material viscosity change when the temperature approaches the glass transition temperature are particularly suited for amorphous polymers. As an example, the work by Nguyen et al. (2008) considers visco-elasticity in a finite deformation framework and the works by Reese et al. (2010) and Srivastava et al. (2010) include thermo-mechanical coupling in models that have been implemented in finite element (FE) analysis packages.

On the contrary, the phase evolution approach is able to describe the physical phenomena taking place during deformation in semi-crystalline polymers. The paper by Westbrook et al. (2010) presents a one-dimensional model based on the concept of phase evolution to quantitatively capture both one-way and two-way shape memory effects in semi-crystalline polymers exhibiting stretch-induced crystallization. Recently, Long et al. (2009) have showed that such a modeling scheme can also be applied to other active polymers, like photo-activated polymers.

Liu et al. (2006) developed a one-dimensional constitutive model where the SMP consists of two phases, a rubbery and a glassy phase, and defined a storage deformation to describe the memory effect. Based on the work by Liu et al. (2006), Chen and Lagoudas (2008a,b) extended the model to a three-dimensional framework. Recently, Qi et al. (2008) developed a three-dimensional finite deformation model for thermo-mechanical behavior of SMPs, based on the evolution of the deformation energy from an entropy- to an enthalpy-based state. Barot and Rao (2006), Barot et al. (2008) applied a similar concept to crystallizable polymers. Volk et al. (2011) performed experimental tensile tests on a high recovery force polyurethane SMP for biomedical applications and introduced a one-dimensional model. Recently, Baghani et al. (2012) have presented a three-dimensional phenomenological model under time-dependent multiaxial thermo-mechanical loadings in the small strain regime.

Motivated by the described framework, the present work focuses on semi-crystalline polymers, in particular, on both low-density (LDPE) and high-density (HDPE) polyethylene-based polymers.

In semi-crystalline polymeric materials, the shape memory behavior manifests itself through thermal retraction on heating when the molecular structure has been oriented by mechanical loads. Such an effect may be considered as a shape memory property since, after a permanent deformation by mechanical loads, polymers may recover their original shape just by thermal actions. In particular, after an imposed strain, which remains fixed as long as temperature is equal or lower than the deformation temperature, if temperature is increased a retraction occurs (or a shrinkage stress arises). In polyethylene-based (PE) polymers, thermo-retraction finds important industrial applications. For example, LDPE and HDPE based films are widely used for packaging processes in which thermal-retraction ensures tight protection and firm containment of goods.

Accordingly, the objectives of the present work are twofold: it aims to experimentally investigate LDPE and HDPE polymers with known compositions, that are being considered for packaging applications, and to introduce a new one-dimensional macroscopic model, discussing its application over a wide range of temperatures and deformations.
Specifically, the first objective of the proposed work is to evaluate the behavior and the characteristics of PE-based SMPs through an uniaxial traction-shrinkage experimental campaign conducted at the Basic Chemicals and Plastics Research Center in Versalis (ENI) (Pachera, 2011; Talamazzi, 2012). Such experimental effort characterizes the orientation process as well as the free and constrained thermal retraction properties of PE-based SMPs, which are of fundamental importance in the design of devices for packaging applications. We investigate both HDPE and LDPE polymers to study the effect of density on material behavior. Moreover, some of the tested LDPE polymers differ in terms of molecular weights to evaluate the effect of weight variation.

The second objective of the present work is to introduce and numerically investigate a new one-dimensional macroscopic model, describing the thermo-mechanical behavior of semi-crystalline polymers, observed experimentally. The aim is to keep the model as much simple as possible for industrial purposes and to provide a preliminary estimation of real material behavior, involving both orientation and thermal retraction of semi-crystalline SMPs.

The idea proposed in the present work is to extend to SMPs modeling and numerical features already introduced and widely accepted for shape memory alloys. The proposed model is thus based on the so-called phase transition approach which introduces internal variables describing the micro-configuration of the material and possibly non-smooth internal constraints, see, e.g., (Frémond, 2002, 2012). The main idea of such an approach is that material properties depend on the microscopic material structure which can be represented by a suitable scalar parameter, the so-called phase parameter, able to describe which kind of microstructure is present. As shape memory in polymers strongly depends on the orientation of the polymers chains, we associate an order parameter to the non-oriented microstructure and we also define a set of parameters capable of describing the mechanical behavior of the material at different temperatures. In particular, we restrict our model to a fixed range of temperatures between the glass transition and the melting temperatures, which is the most significant from the industrial point of view.

Hence, by using general thermo-mechanical laws, we recover a system of constitutive relations coming from energy and dissipation functionals, chosen on the basis of the obtained experimental evidences. Moreover, the model is formulated in a finite strain framework to account for the large deformations reached during the experimental campaign. We assume that no viscosity appears and that phase evolution is rate-independent.

Thanks to the introduction of suitable phase variables, we could include in our model the typical phenomenon of crystallization in semi-crystalline polymers, which represents a microscopic configuration change taking place at certain temperatures and therefore can be described as a phase transformation. However, we are now restricting our analysis to the case when the amount of crystallized chains is fixed and thus we are concentrating on the orientation of the chains in the amorphous phase.

We conduct the numerical investigation of the proposed model through an effective and efficient computational procedure, introduced in the framework of crystal plasticity by Schmidt-Baldassari (2003) and of shape memory alloys by Bartel and Hackl (2009, 2010), Bartel et al. (2011), Kiefer et al. (2012), Auricchio et al. (2014). It consists in replacing the Kuhn–Tucker complementarity inequality conditions by the equivalent Fischer–Burmeister complementarity function (Fischer, 1992) and in making possible to omit an active set search, which is an advantage when dealing with several variable constraints as in the proposed model.

Additionally, the proposed work presents several numerical results for uniaxial traction-shrinkage tests and a comparison between numerical predictions and experimental results, in order to show the capability of the model to qualitatively and quantitatively reproduce basic effects such as orientation processes, free and constrained thermal retraction tests.

The paper is organized as follows. Section 2 focuses on the experimental campaign. Then, Sections 3 and 4 present the one-dimensional macroscopic model and its numerical counterpart. Section 5 qualitatively and quantitatively investigates the proposed model and compares numerical predictions to experimental results. Conclusions and summary are finally given in Section 6.

### 2. Experimental campaign

The present section describes an experimental campaign conducted at the Basic Chemicals and Plastics Research Center in Versalis (ENI), on commercial LDPE and HDPE polymers (Pachera, 2011; Talamazzi, 2012).

Table 1 lists the property values of the tested materials, which differ in terms of density and molecular weight. In particular, we conduct some experimental tests on one type of LDPE polymers (Mat. A) and one type of HDPE polymers (Mat. E) to

<table>
<thead>
<tr>
<th>Property</th>
<th>Mat. A</th>
<th>Mat. B</th>
<th>Mat. C</th>
<th>Mat. D</th>
<th>Mat. E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt flow index (MFI) (190 °C, 2.16 kg) (g/10 min)</td>
<td>0.79</td>
<td>0.80</td>
<td>2.20</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.9221</td>
<td>0.9230</td>
<td>0.9230</td>
<td>0.922</td>
<td>0.939</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>50.00</td>
<td>47.47</td>
<td>47.30</td>
<td>47.54</td>
<td>70.00</td>
</tr>
<tr>
<td>Melting point (T_m) (°C)</td>
<td>110.1</td>
<td>113.0</td>
<td>113.0</td>
<td>112.0</td>
<td>129.0</td>
</tr>
<tr>
<td>Weight average molecular weight (Mw) (KDa)</td>
<td>-</td>
<td>170</td>
<td>145</td>
<td>220</td>
<td>-</td>
</tr>
</tbody>
</table>
evaluate the effect of density variation on material behavior; then, we conduct some tests on three types of LDPE polymers (Mat. B–D) to consider the effect of molecular weight variation on material behavior.

All the specimens are cut in the form of $100 \times 9 \times 0.2$ mm rectangular strips, from compression molded sheets. Compression molding is carried out by means of a Saspol press (see Fig. 1) in a frame-type mold ($200 \times 200 \times 0.2$ mm), with the following cycle: pre-heating at $170^\circ C$ for 10 min with no applied pressure; 2 min with a pressure of 15 bars; 3 min at 50 bars; cooling down at $10^\circ C$/min. During the cooling stage the pressure does not act on the material, whose volume is decreasing, but simply keeps the mold closed. Therefore, the choice of the frame-type mold ensures the state of isotropy of the final molded sheet, that has been also verified during the free thermal retraction test described in the following.

2.1. Orientation test

Material orientation under isothermal conditions (at temperatures below the melting temperature, $T_m$) is realized by using a tensile testing machine, Instron series 4505, equipped with a temperature chamber (see Fig. 2). Each specimen is fixed into the machine grips and subjected to a constant displacement-rate tensile test run, in which it is possible to set the following variables:

- initial grip distance (fixed at 15 mm);
- maximum imposed elongation;
- testing temperature;
- crosshead speed (fixed at 9 mm/min).

The orientation test consists of the following steps:

1. the crosshead moves at a fixed speed until the maximum imposed elongation is reached;
2. after reaching the required elongation, the crosshead moves in the opposite direction at the same speed, thus allowing the specimen to recover a partial deformation until it reaches a stable thermodynamic state at zero stress. No hold time is kept between the loading and unloading phases to avoid the stress relaxation phenomenon due to material viscoelasticity.

Fig. 3(a) and (c) present the orientation curves in terms of engineering stress, $\sigma$, and engineering strain, $\varepsilon$, at temperatures of 26, 30, 45, 60, 75 and $90^\circ C$ and maximum imposed deformation of 600%, for materials A and E, respectively. Fig. 3(b) and (d) shows the orientation curves in terms of engineering stress, $\sigma$, and engineering strain, $\varepsilon$, at a constant temperature of $60^\circ C$ and maximum imposed deformations of 10%, 25%, 50%, 100%, 200%, 400% and 600% for materials A and E, respectively.

As it can be observed from Fig. 3(a) and (c), the material is first deformed in the elastic region, characterized by increasing slope and yield stress and by decreasing yield strain with decreasing temperature. At high temperatures, in fact, the macromolecular chains have more freedom to move; thus, the deformation at a given stress in the elastic region increases with increasing temperature (the slope decreases). Similarly, at high temperatures the yield stress decreases. Then, after reaching the yield stress, the plastic deformation phase starts, giving rise to the orientation of the molecular structure. Upon unloading, the material reaches a residual strain at zero stress, as equilibrium thermodynamic state for a given temperature. The slope of the curve upon unloading and the residual strain increase with decreasing temperature.

Fig. 1. Saspol press (left) and zoom of the plates (right).
As it can be observed from Fig. 3(b) and (d), the slope of the curve upon unloading decreases with increasing imposed deformation, while the residual deformation increases. In fact, if the imposed deformation is low, material behavior remains elastic; upon unloading, the deformation is completely recovered. On the contrary, with increasing imposed deformation, material behavior is no more elastic and residual deformation increases. We already remark that, if temperature is increased after unloading, the material is no more in an equilibrium state and thermal retraction effect is manifested.

Materials A (LDPE) and E (HDPE) present a similar trend, but also some differences:

- the slope in the elastic region is higher in material E which presents a lower amorphous part than material A;
- material E presents a higher yield stress and a transition zone around the yield stress from a maximum stress to a lower stress before reaching a plateau. This aspect is explained by the phenomenon of necking, not manifesting in material A which shows a gradual transition from the elastic to the plastic zone;
- upon unloading, the recovered strain is higher in material A than material E, consequence of the fact that material E has a lower elastic part to recover.

We would like to remark that the obtained results are in accordance with those provided by Hong et al. (2004), who studied stress–strain relationships in step-cycle experiments.

Fig. 3(e) shows the orientation curves in terms of engineering stress, $\sigma$, and engineering strain, $e$, at a constant temperature of 60 °C and maximum imposed deformation of 600% for materials B–D. As it can be observed, material behavior is equivalent.

2.2. Constrained thermal retraction test

All the specimens, oriented as described in Section 2.1, are subjected to a constrained thermal retraction test. The test is carried out by using a rheometer ARES LS II (see Fig. 4), equipped with a temperature cell, able to measure the force generated by the specimen when subjected to heating at constrained deformation.

The constrained thermal retraction test consists of the following steps:

1. the specimen is oriented at a predefined temperature and imposed deformation;
2. the specimen is placed inside the temperature cell and clamped between grips (see Fig. 4). After a few minutes at an initial temperature of 30 °C, the grip distance is adjusted to avoid sagging of the specimen (due to the small thermal dilatation from room temperature to 30 °C) and after that, the grip distance remains unchanged for the whole test.
3. the temperature is increased from the initial temperature to a value above the melting temperature, $T_m$, at a rate of 2 °C/min. As temperature increases, the specimen tries to shrink in order to reach a thermodynamic equilibrium state. Due to the constraint, the specimen generates a force of entropic nature, due to the tendency of the oriented macromolecular chains to reach a state of thermodynamic equilibrium.
Fig. 5(a) and (c) present the constrained thermal retraction curves in terms of true stress, \( r \), and temperature, \( T \), for materials A and E, oriented at temperatures of 26; 30; 60; 75 and 90 °C and maximum imposed deformation of 600%; (b)–(d) at constant temperature of 60 °C and different imposed deformations of 10; 25; 50; 100; 200; 400 and 600%. (e) Curves for materials B–D at a temperature of 60 °C and maximum imposed deformation of 600%.

Fig. 5(a) and (c) present the constrained thermal retraction curves in terms of true stress, \( r \), and temperature, \( T \), for materials A and E, oriented at temperatures of 26; 30; 60; 75 and 90 °C and maximum imposed deformation of 600%; (b)–(d) at constant temperature of 60 °C and different imposed deformations of 10; 25; 50; 100; 200; 400 and 600%. (e) Curves for materials B–D at a temperature of 60 °C and maximum imposed deformation of 600%.

As it can be observed from Fig. 5(a) and (c), the stress increases until a maximum value and then decreases until a zero value at the melting temperature, \( T_m \), where material loses its original shape. In particular, the slope of the curve increases until the orientation temperature is reached and the maximum value of the stress increases with decreasing orientation temperature. From Fig. 5(b) we observe that the maximum value of the shrinkage stress is greater at an orientation strain of 400% than at 200%, but becomes smaller for an imposed strain of 600%. Again, materials A (LDPE) and E (HDPE) present a similar trend, however material E exerts higher stresses than material A.

Fig. 5(d) shows the comparison between the experimental curves in terms of true stress, \( r \), and temperature, \( T \), for materials B–D oriented at a temperature of 60 °C and maximum imposed deformation of 600%. As it can be observed, material behavior is again equivalent.
2.3. Free thermal retraction test

All the specimens, oriented as described in Section 2.1, are also subjected to a free thermal retraction test. The test is carried out by using a rheometer ARES LS II (see Fig. 4), equipped with a temperature cell.

The free thermal retraction test consists of the following steps:

1. the specimen is oriented at a predefined temperature and imposed deformation;
2. the specimen is placed inside the temperature cell and clamped between grips (see Fig. 4). After a few minutes at an initial temperature of 30 °C, the rheometer is put in load-control mode and instructed to keep the load at a very small constant tensile level (a few grams). Such a prescribed load is by far too small to cause appreciable deformation of the specimen, but it acts as a set-point, ensuring that the grip distance is automatically and continuously adjusted during the test to match the actual specimen length which will decrease on heating due to thermal shrinkage;

3. the test is then conducted by heating up at a rate of 2 °C/min. The oriented specimen, under these test conditions, undergoes a virtually unconstrained thermal shrinkage (the maximum reduction in length at a given temperature is checked to be equal to that obtained in a free thermal shrinkage test performed by immersing the specimen in an heated silicone oil bath). Our test setup, taking advantage of the load-control mode of the instrument, allows the direct measurement of the specimen length as a function of temperature during the thermal-shrinkage process.

Fig. 6(a) and (c) present the free thermal retraction curves in terms of shrinkage, and temperature, \( T \), for materials A and E oriented at temperatures of 26, 30, 60 and 90 °C and maximum imposed deformation of 600%, respectively. Fig. 6(b) shows the free thermal retraction curves in terms of shrinkage and temperature, \( T \), for material A oriented at a temperature of 60 °C and three imposed deformations of 200%, 400% and 600%.

As it can be observed from Fig. 6(a) and (c), the retraction process begins at the orientation temperature and the maximum value of the shrinkage is reached at the melting temperature, \( T_m \). Moreover, as shown in Fig. 6(b), the maximum value of the shrinkage increases with increasing imposed strain. In such a test, the curve related to material E (HDPE) at low temperatures is below the curve of material A (LDPE), while, around \( T_m \), the slope of the curve increases and reaches a maximum value of the shrinkage which is greater for material E.

Fig. 6(d) shows the comparison between the experimental curves in terms of shrinkage and temperature, \( T \), for materials B–D oriented at a temperature of 60 °C and maximum imposed deformation of 600%. Again, material behavior is equivalent.

2.4. Tests above the melting temperature

From the results related to materials B–D, presented in Figs. 3(e), 5(d) and 6(d), it is clear that the molecular weight has no influence on material behavior at temperatures below the melting temperature, \( T_m \). Consequently, we investigate the behavior of such materials in the molten state (Talamazzi, 2012).

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**Fig. 6.** Experimental free thermal retraction test: curves in terms of shrinkage and temperature, \( T \), Curves for specimens of materials A and E, oriented (a)–(c) at different temperatures of 26, 30, 60 and 90 °C and maximum imposed deformation of 600%; (b) at a temperature of 60 °C and different imposed deformations of 200%, 400% and 600%. (d) Curves for specimens of materials B–D oriented at a temperature of 60 °C and maximum imposed deformation of 600%.
Fig. 7(a) shows the melt viscosity versus shear rate curves measured by means of a capillary rheometer (Goettfert) at a temperature of 190 °C. The three materials exhibit different melt viscosities, as it can be expected on account of the different values of weight average molecular weight (see Table 1). A blown film extrusion line (Sterling) is set for processing the three materials B–D. To ensure that the materials undergo the same strain and strain rate history during the film production process, we take care that the important parameters governing the process kinematics are controlled. In particular, we keep constant, for the three materials the following process parameters:

- all process temperatures;
- total throughput, in terms of mass per unit time;
- take-up ratio (TUR), defined as the ratio of film velocity at the nip roll to average velocity of film leaving the die;
- blow-up ratio (BUR), defined as the ratio of final film-tube diameter to die diameter;

We then perform the thermal retraction tests on specimens cut parallel to the extrusion direction (machine direction, MD) from the obtained films, which are therefore oriented in the molten state, i.e. at \( T > T_m \), under the same temperature, strain and strain rate conditions. Fig. 7(b) shows the comparison between the experimental curves in terms of true stress, \( \sigma \), and temperature, \( T \). As it can be observed, under the imposed temperature ramp (2 °C/min) stress is zero until temperature approaches the melting temperature, \( T_m \); then, it sharply rises to a maximum which is not far from \( T_m \); and finally, it comes back to zero. An important result is the fact that stresses obtained by orienting the specimens below \( T_m \) are higher than those obtained by orienting above \( T_m \), as shown in Figs. 5(d) and 7(b).

3. A new one-dimensional phenomenological model for shape memory polymers

This section addresses a new one-dimensional phenomenological model for SMPs, based on the so-called phase transition approach. In the following, we present the model formulation in the time-continuous framework and a physical interpretation of model parameters. As pointed out in Section 1, the proposed model is introduced to simply provide a preliminary estimation of the material behavior observed experimentally, for industrial purposes. Therefore, the forms of the functionals proposed in the following (i.e., the free-energy and dissipation functions) are chosen on the basis of the experimental evidences previously described.

3.1. Model formulation

In the framework of macroscopic modeling and of finite strain continuum mechanics, we assume the axial stretch, \( \lambda \), as the main kinematic variable, and the temperature, \( T \), as state variable. A general assumption of multiplicative split of the axial stretch is adopted in the form (de Souza Neto et al., 2008):

\[
\lambda = \lambda^e \lambda^i
\]

where \( \lambda^e \) and \( \lambda^i \) denote the axial elastic and inelastic stretch, respectively. After defining the axial total, elastic and inelastic logarithmic strains (denoted with \( \varepsilon \), \( \varepsilon^e \) and \( \varepsilon^i \), respectively) as:

\[
\begin{align*}
\varepsilon &= \ln \lambda \\
\varepsilon^e &= \ln \lambda^e \\
\varepsilon^i &= \ln \lambda^i
\end{align*}
\]

Fig. 7. Tests above the melting temperature, \( T_m \), on materials B–D. (a) Melt viscosity versus shear rate curves measured by capillary rheometry at 190 °C; (b) constrained thermal retraction tests (see Section 2.2), performed on blown films specimens cut in extrusion direction.
we rewrite Eq. (1), as follows:
\[
\varepsilon = \varepsilon^e + \varepsilon^e
\]  
(3)

Recalling the discussion of Section 1, the phenomenon of thermal retraction in PE-based polymers is a shape memory property and it is strongly connected with molecules orientation under mechanical and thermal loads. Thus, in the phase transition framework, the main idea is that the microscopic structure of the polymer can be represented by a suitable scalar parameter, the so-called phase parameter, able to describe which kind of microstructure is present. In order to introduce a suitable phase parameter, we start by viewing the semi-crystalline polymer as composed of chains of type A, which are in the crystalline phase, and chains of type B, which are in the amorphous phase and can be (non)oriented by mechanical or thermal loads. Then, as shape memory in semi-crystalline polymers strongly depends on the orientation of the polymer chains, we assume the state variable, η, as a phase parameter describing the non-oriented microstructure and related to the local proportion of non-oriented chains of type B with respect to the oriented phase. Due to its physical meaning, the phase parameter has to be between 0 and 1, i.e., η ∈ [0, 1]. In particular, the case η = 1 corresponds to the presence of completely non-oriented chains, while the case η = 0 stands for complete ordered chains.

We choose the inelastic logarithmic strain, \( \varepsilon^e = \varepsilon^e(T, \eta) \), as follows:
\[
\varepsilon^e = C_s \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \eta)
\]  
(4)

with \( C_s \) and \( \alpha \) positive material parameters and \( T_0 \) a reference temperature.

### 3.1.1. Helmholtz free-energy function

The Helmholtz free-energy function, \( \Psi = \Psi(\varepsilon, T, \eta) \), is assumed in the following classical form:
\[
\Psi = \frac{1}{2}E(\varepsilon^e)^2 - c_s T \ln T + I_{0.1}(\eta)
\]  
(5)

that, after introducing Eq. (3), becomes:
\[
\Psi = \frac{1}{2}E(\varepsilon - \varepsilon^e)^2 - c_s T \ln T + I_{0.1}(\eta)
\]  
(6)

where \( c_s > 0 \) is the specific heat (assumed constant for the sake of simplicity) and \( I_{0.1}(\eta) \) is the indicator function forcing to fulfill the constraints on \( \eta \), defined as (Nguyen and Moumni, 1995a,b):
\[
I_{0.1}(\eta) = \begin{cases} 
0 & \text{if } 0 \leq \eta \leq 1 \\
+\infty & \text{otherwise}
\end{cases}
\]  
(7)

The function \( E = E(T, \eta) \) represents the Young’s modulus, that, according to experimental evidences of Fig. 3(a)–(d), we assume to strongly depend on temperature, \( T \), and on phase, \( \eta \), as follows:
\[
E = \exp \left[ \frac{\beta}{T - T_0} \right] \frac{1}{1 + \frac{1}{\eta}}
\]  
(8)

\( E_1 \) and \( E_0 \) being positive parameters due to material rigidity for the two cases \( \eta = 1 \) and \( \eta = 0 \), respectively (with \( E_1 > E_0 \)), and \( \beta \) a positive material parameter. In particular, we assume that at constant temperature, \( T \), the Young’s modulus depends on the phase, \( \eta \), following the classical model of Reuss, while at constant phase, \( \eta \), the Young’s modulus depends exponentially on temperature, \( T \), as manifested in Fig. 3(a)–(d). The reader is referred to Appendix A for a discussion on the adopted expression for the Young’s modulus.

### 3.1.2. Constitutive equations

Starting from the free-energy, \( \Psi \), presented in Eq. (6), and following standard arguments (de Souza Neto et al., 2008), we derive the Kirchhoff axial stress, \( \tau \):
\[
\tau = \frac{\partial \Psi}{\partial \varepsilon} = E(\varepsilon - \varepsilon^e) = \exp \left[ \frac{\beta}{T - T_0} \right] \frac{1}{1 + \frac{1}{\eta}} \left( \varepsilon - C_s \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \eta) \right)
\]  
(9)

as well as the thermodynamic force, \( X^{nd} \), governing the evolution of \( \eta \):
\[
X^{nd} = -\frac{\partial \Psi}{\partial \eta} = -\frac{1}{2} \frac{\partial E}{\partial \eta} (\varepsilon - \varepsilon^e) + E(\varepsilon - \varepsilon^e) \frac{\partial \varepsilon^e}{\partial \eta} - \gamma = -\frac{1}{2} \frac{\partial E}{\partial \eta} \varepsilon^2 + \frac{\partial \varepsilon^e}{\partial \eta} \tau - \gamma
\]
\[
= -\frac{1}{2} \exp \left[ \frac{\beta}{T - T_0} \right] \frac{(E_1 - E_0)E_1E_0}{(E_0 + E_1(1 - \eta))^2} \left( \varepsilon - C_s \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \eta) \right)^2
\]
\[
- C_s \exp \left[ \frac{\alpha + \beta}{T - T_0} \right] \frac{1}{1 + \frac{1}{\eta}} \left( \varepsilon - C_s \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \eta) \right) - \gamma
\]  
(10)
Here, $\gamma \in \partial I_{[0,1]}(\chi)$, with $\partial I_{[0,1]}(\chi)$ the subdifferential of the indicator function $I_{[0,1]}(\chi)$, taken in the sense of convex analysis (Brézis, 1973):

$$\partial I_{[0,1]}(\chi) = \begin{cases} \gamma^0 \leq 0 & \text{if } \chi = 0 \\ 0 & \text{if } 0 < \chi < 1 \\ \gamma^1 \geq 0 & \text{if } \chi = 1 \end{cases}$$ (11)

We can associate to Eq. (11) the classical Kuhn–Tucker complementarity conditions, as follows:

$$\begin{cases} \chi \geq 0, \gamma^0 \leq 0, \gamma^0 \chi = 0 \\ (\chi - 1) \leq 0, \gamma^1 \geq 0, \gamma^1(\chi - 1) = 0 \end{cases}$$ (12)

### 3.1.3. Evolution equations and limit functions

We define a limit function, $F = F(X^{nd}, T)$, playing the role of yield function (Lubliner, 1990), in the following form:

$$F = \frac{X^{nd}}{2} - \frac{\eta}{2}$$ (13)

where $\eta = \eta(T, \chi)$ is a sufficiently smooth function, governing the yield level of stress activating the phase transition, i.e., the orientation process:

$$\eta = C_\eta \exp \left[ \frac{E_0}{T - T_0} \right] + h_1 \exp \left[ \frac{E_{h_1}}{T - T_0} \right] (1 - \chi) + h_2 \exp \left[ \frac{E_{h_2}}{T - T_0} \right] (1 - \chi)^2 + h_3 \exp \left[ \frac{E_{h_3}}{T - T_0} \right] (1 - \chi)^3$$ (14)

$C_\eta$ and $E_0$ being positive material parameters and $h_1, h_2, h_3, E_{h_1}, E_{h_2},$ and $E_{h_3}$ positive material constants describing material hardening.

Then, as traditionally done in the context of associative evolution, we assume the evolution equation of $\chi$, as follows:

$$\dot{\chi} = \xi \frac{X^{nd}}{X^{nd} + \frac{\eta}{2}}$$ (15)

where $\xi$ is a non-negative consistency parameter.

The model is finally completed by the classical Kuhn–Tucker conditions, as follows:

$$\xi \geq 0; \ F \leq 0; \ \dot{\xi} F = 0$$ (16)

### 3.1.4. Dissipation function

Although the proposed model relies on an yield surface-based formulation, we complete the description by recalling that the yield surface condition (13) can be equivalently converted in a pseudo-potential of dissipation, $\phi = \phi(\chi, T)$, which is a positive convex functional depending on dissipative variables, vanishing for vanishing dissipation, in particular in the form:

$$\phi = \begin{cases} -\eta \chi & \text{if } \chi \leq 0 \\ 0 & \text{if } \chi > 0 \end{cases}$$ (17)

We remark that, once defined the pseudo-potential of dissipation, $\phi$, we can prescribe the constitutive relation for the internal force, $X$, responsible for the phase transition, as follows (Frémond, 2002; Frémond, 2012; Gurtin et al., 2010; Halphen and Nguyen, 1975, 1974):

$$X = -X^{nd} + X^d = \frac{\partial \Psi}{\partial \chi} + \frac{\partial \phi}{\partial \chi}$$ (18)

In particular, two contributions are considered, i.e., a non-dissipative term, $X^{nd}$, and a dissipative term, $X^d$. The constitutive relation for the internal non-dissipative force, $X^{nd}$, is given in Eq. (10), while the constitutive relation for the dissipative force, $X^d$, is:

$$X^d = \frac{\partial \phi}{\partial \chi} = \begin{cases} -\eta & \text{if } \chi \leq 0 \\ 0 & \text{if } \chi > 0 \end{cases}$$ (19)

From the definition of $X$, presented in Eq. (18), we can then derive the limit function introduced in Eq. (13). We note that such an approach, similar to that employed in shape memory alloy modeling, considers a translation of the thermodynamic force, $X^{nd}$, to allow the phase transformation in the thermal retraction case for which $X^{nd} = 0$, i.e., $\tau = 0$.

Therefore, the evolution of the phase, $\chi$, depends on the internal force, $X$, which is included in the energy balance of the system. We obtain the following balance equation:

$$X = -X^{nd} + X^d = 0$$ (20)
after assuming that no micro-forces are applied to activate the orientation of polymer chains. From Eq. (20) we can derive the evolution equation of the phase parameter, $\chi$, as follows:

$$\dot{\chi} = \partial_l \eta_0 \chi^{n_d}$$

that can then rewritten as Eq. (15).

3.1.5. Physical interpretation of model parameters

Ideally, the identification procedure of a material model should be automated using optimization techniques. In the following sections, all model parameters are calibrated through a trial and error procedure to best fit the experimental orientation curves of Fig. 3(a) and (c), related to materials A and E.

In the present section, however, we comment, whenever possible, on model parameters physical interpretation. We consider the one-dimensional diagram of Fig. 8(a), generated by the model, in terms of Kirchhoff stress, $\tau$, and logarithmic strain, $\varepsilon$, where all the quantities of interests are reported.

In the following, we derive all the general equations for the simple case of Fig. 8(a). Then, we simplify such equations by assuming the hardening parameters, introduced in Eq. (14), equal to zero and a material rigidity, $E' = E_1 = E_0$, equal for the two cases $\chi = 1$ and $\chi = 0$ (see Fig. 8(b)).

The material starts from the reference configuration at a given temperature and zero stress in the amorphous state, i.e., $\chi = 1$ (points A and A' of Fig. 8(a)–(b)).

If a load is applied and then increased, material behavior is at first linearly elastic with slope, $k_i$, which increases with decreasing temperature, $T$, as follows:

$$k_i = \exp \left[ \frac{\beta}{T - T_0} \right] E_1$$

If we assume a constant material parameter, $E'$, the slope becomes (see Fig. 8(b)):

$$k' = \exp \left[ \frac{\beta}{T - T_0} \right] E'$$

According to Eq. (13), the material stays in equilibrium for $\dot{\chi} = 0$ till $X^{n_d} = -\eta$. Thus, when $X^{n_d} = -\eta$, the strain reaches an elastic limit value, $\varepsilon_l$ (point B of Fig. 8(a)). After substituting Eq. (10) into Eq. (13) and assuming $\varepsilon = \varepsilon_l$, the elastic limit strain, $\varepsilon_l$, is solution of the following equation:

$$\exp \left[ \frac{\beta}{T - T_0} \right] (E_1 - E_0) \varepsilon_l^2 + C_2 \exp \left[ \frac{\alpha + \beta}{T - T_0} \right] E_1 \varepsilon_l = C_q \exp \left[ \frac{E_0}{T - T_0} \right]$$

The elastic limit stress, $\tau_l$, follows:

$$\tau_l = E \varepsilon_l = \exp \left[ \frac{\beta}{T - T_0} \right] E_1 \varepsilon_l$$

If we assume a constant material parameter, $E'$, the elastic limit strain and stress result (point B' of Fig. 8(b)):

$$\left\{ \begin{array}{l} \varepsilon_l' = \frac{C_2}{C_q} \frac{1}{T} \exp \left[ \frac{E_0 - \beta \varepsilon_l}{T - T_0} \right] \\ \tau_l' = \frac{C_2}{C_q} \exp \left[ \frac{E_0 - \beta \varepsilon_l}{T - T_0} \right] \end{array} \right.$$

![Fig. 8.](image) (a) 1D diagram in terms of Kirchhoff stress, $\tau$, and logarithmic strain, $\varepsilon$, generated by the proposed model. (b) Simplified 1D diagram, generated by assuming the hardening parameters, introduced in Eq. (14), equal to zero and a material rigidity, $E' = E_1 = E_0$, equal for the two cases $\chi = 1$ and $\chi = 0.$
Since experimental evidences of Fig. 3(a)–(d) shows that the elastic limit strain decreases with decreasing temperature and the elastic limit stress increases with decreasing temperature, we derive the following constraints on model parameters from system of Eqs. (26):

\[
\begin{cases}
E_n < \alpha + \beta \\
E_n > \alpha
\end{cases}
\]

(27)

If the load further increases, inelastic deformations start to develop and the orientation process starts. As it can be observed, the hardening parameters are responsible for the stress–strain curve between points B and C of Fig. 8(a). The choice of \( \eta \) reported in Eq. (14) is due to experimental observations. Once the imposed level of load is reached, the orientation process reaches a certain level of orientation (point C of Fig. 8(a)), where \( \chi = \chi_i \) and \( \varepsilon = \varepsilon_i \). In the particular case of completed orientation process, i.e., \( \chi = \chi_i = 0 \), the maximum transformation strain, \( \varepsilon_{\text{max}} \), is reached. If we assume a constant material parameter, \( E^* \), and no hardening (i.e., inelastic deformations start to develop at constant elastic limit stress, \( \tau_1 \)), the maximum transformation strain becomes:

\[
\varepsilon_{\text{max}} = \frac{C_\eta}{C_x^*} E^* \exp \left[ \frac{E_n - \alpha - \beta}{T - T_0} \right] + C_v \exp \left[ \frac{\alpha}{T - T_0} \right]
\]

(28)

and increases with decreasing temperature, \( T \), thus reproducing experimental evidences of Fig. 3(a)–(d).

If we start to unload from point C of Fig. 8(a), we evolve in the region for which \( \chi = 0 \). The slope upon unloading, \( k_f \), follows:

\[
k_f = \exp \left[ \frac{\beta}{T - T_0} \right] \frac{1}{\frac{1}{\eta} + \frac{1}{\varepsilon_i}}
\]

(29)

and increases with decreasing temperature, \( T \), and with increasing \( \chi \), as experimentally observed in Fig. 3(a)–(d). If we assume a constant material parameter, \( E^* \), the slope upon unloading becomes (point \( C^* \) of Fig. 8(b)):

\[
k^* = \exp \left[ \frac{\beta}{T - T_0} \right] E^*
\]

(30)

Upon unloading, when \( \tau = 0 \) and thus \( X^\text{nd} = 0 \), a residual strain, \( \varepsilon_{\text{res}} = \varepsilon_{\text{res}}^0 \), is present (points D and \( D^* \) of Fig. 8(a)–(b)), in the following form:

\[
\varepsilon_{\text{res}} = C_x \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \chi_i)
\]

(31)

which increases with decreasing temperature, \( T \), and phase, \( \chi \).

If we start increasing temperature from point \( D \) of Fig. 8(a) at \( \tau = 0 \) and no constraints on the material (free thermal retraction), the residual strain, \( \varepsilon_{\text{res}} \), can be partially recovered.

On the other hand, if we start increasing temperature at fixed \( \varepsilon = \varepsilon_{\text{res}} \) from point D of Fig. 8(a) (constrained thermal retraction), we obtain, after assuming a constant material parameter, \( E^* \):

\[
\begin{cases}
\tau = E^* \exp \left[ \frac{\eta}{T - T_0} \right] \left( \varepsilon_{\text{res}} - C_x \exp \left[ \frac{\alpha}{T - T_0} \right] (1 - \chi_i) \right) \\
X^\text{nd} = -C_x \exp \left[ \frac{\alpha}{T - T_0} \right] \tau
\end{cases}
\]

(32)

Moreover, we observe that at point D, we have \( \chi > 0 \) and this last remark justifies irreversibility of the retraction process at \( \tau = 0 \).

4. Time-discrete framework

We now elaborate on a possible algorithmic treatment of model equations. For the sake of notation simplicity, we use superscript \( n \) for all the variables evaluated at time \( t_n \), while we drop superscript \( n + 1 \) for all the variables computed at time \( t_{n+1} \).

We start making use of a classical backward-Euler integration algorithm for the evolution Eq. (15). In this sense, the time-discretized evolution equation is given by:

\[
\chi_n - \chi_{n-1} - \Delta \chi \frac{X^\text{nd} + \frac{n}{2}}{X^\text{nd} + \frac{n}{2}} = 0
\]

(33)

where \( \Delta \chi = \int_{t_n}^{t_{n+1}} \dot{\chi} \, dt \) is the time-integrated consistency parameter.

In the model, since we deal with one phase parameter involving constraints, we adopt the approach consisting in the replacement of the Kuhn–Tucker complementarity inequality conditions, \( a \leq 0, b \geq 0, ab = 0, a, b \in \mathcal{R} \), by the equivalent Fischer–Burmeister complementarity function \( \Phi \) (Fischer, 1992), with \( \Phi : \mathcal{R}^2 \rightarrow \mathcal{R} \) and defined as follows:
\[ \Phi(a, b) = \sqrt{a^2 + b^2} - a - b, \] such that \[ \Phi(a, b) = 0 \iff a \leq 0, \ b \geq 0, \ ab = 0. \] Such a definition allows to rewrite the complementarity inequality constraints as a non-linear equality constraint through the application of the Fischer–Burmeister complementarity function. Therefore, we substitute the discrete Kuhn–Tucker conditions deriving from Eq. (16) by the following function in the time-discrete frame:

\[ \sqrt{F^2 + \Delta z^2} + F - \Delta z = 0 \]  \quad (34)

The same strategy can be employed to treat the set of inequalities given by the constraint on \( \chi \). In fact, the additional Kuhn–Tucker conditions (12) can be substituted by the equivalent conditions:

\[
\begin{align*}
\sqrt{\chi^2 + (\gamma^0)^2} + \gamma^0 - \chi &= 0 \\
(\chi - 1)^2 + (\gamma^1)^2 + (\chi - 1) - \gamma^1 &= 0
\end{align*}
\]  \quad (35)

The time-discrete problem, \( Q = Q(\alpha, \mathbf{h}) \), evaluated at time \( t_{n+1} \), takes the specific form:

\[
Q = \begin{bmatrix}
\chi - \chi_n - \Delta \chi^0 \frac{\chi^0}{\sqrt{\chi^0 + 1}} \\
\sqrt{F^2 + \Delta z^2} + F - \Delta z \\
\sqrt{(\chi - 1)^2 + (\gamma^1)^2} + (\chi - 1) - \gamma^1
\end{bmatrix}
\]  \quad (36)

with \( \mathbf{h} = \{ \chi, \Delta z, \gamma^0, \gamma^1 \} \). The active set can now be determined via the solution of the following non-linear system of equations:

\[
Q = 0
\]  \quad (37)

by using a classical Newton–Raphson method.

All the model equations and numerical examples presented in Section 5 are implemented in two Mathematica (Wolfram, 2013) packages, AceGen and AceFEM (Korelc, 2009). These systems allow to automatically obtain explicit expressions resulting from differentiation. In particular, the tangent matrix is computed analytically and factorized at each iteration. This leads to a quadratic convergence rate of the Newton method (Quarteroni et al., 2007). In Appendix B we provide the tangent matrix deriving from the time-discrete problem (36).

We remark that, since the Fischer–Burmeister complementary function, \( \Phi \), is non-differentiable at \((0,0)\), we make use of a regularized counterpart, \( \Phi_\delta \), defined as \( \Phi_\delta(a, b, \delta) = \sqrt{a^2 + b^2 + 2\delta^2} + a - b \), such that \( \Phi_\delta(a, b, \delta) = 0 \iff a \leq 0, \ b \geq 0, \ ab = -\delta^2 \), where \( \delta \) is a positive regularization parameter (Kanzow, 1996).

5. Numerical results

In this Section we test the validity of the proposed model as well as its algorithm through some numerical simulations and comparisons with experimental results described in Section 2. The purpose is to emphasize model prediction capabilities through a qualitative and then quantitative validation with experimental data.

All the results presented in the following are expressed in terms of engineering stresses and strains. The derivation of engineering stresses from the Kirchhoff stress, \( \tau \), defined in Eq. (9), is possible under the hypothesis of material incompressibility, which is valid for the material under investigation (Hiss et al., 1999).

In all the numerical tests we adopt the material parameters reported in Table 2. Here, parameters are calibrated through a trial and error procedure on experimental orientation curves of Fig. 3(a) and (c), related to materials A and E, by starting from the physical interpretation given in Section 3.1.5.

5.1. Orientation test

We start by simulating the orientation test on materials A and E, shown in Fig. 3(a)-(d), as simple uniaxial tension test, with displacement control and prescribed homogeneous constant temperature field. We first consider constant temperatures of 26, 30, 45, 60, 75 and 90 °C and maximum imposed deformation of 600%; then, we consider a constant temperature of 60 °C and imposed deformations of 10%, 25%, 50%, 100%, 200%, 400% and 600%. Fig. 9(a)-(d) shows the comparison between predicted and experimental curves, in terms of stress, \( \sigma \), and strain, \( e \). As it can be observed, the model successfully predicts the experimental curves for both LDPE and HDPE polymers, thus demonstrating its flexibility in capturing the behavior of PE-based polymers with different densities. We remark that the experiments show a concave curve during unloading due to the viscoelastic behavior of the investigated material, which is not taken into account by the present formulation. However, the values of the residual deformations are well predicted by the model, as shown in Fig. 9(a) and (c). Moreover, the experimental softening of Fig. 3(c) is not reproduced by the model.
As expected, model quantities, $k$, $k_f$, $\tau_i$, and $\varepsilon_m$, introduced in Section 3.1.5, increase with decreasing temperature, while $\varepsilon_0$ decreases (see Fig. 10).

### 5.2. Constrained thermal retraction test

Due to difficulties in the simulation of all the steps of the experimental constrained thermal retraction test (see Section 2.2), we make a qualitative interpretation of such a test for numerical purposes. In particular, we simulate the test as simple uniaxial tension test, with displacement control and prescribed homogeneous constant temperature field. Upon unloading, at zero stress, we fix the residual strain and we start increasing the temperature until a value above the melting temperature, $T_m$. Fig. 11(a) and (b) shows the qualitative model response for a specimen orientated at a temperature of 26°C and maximum deformation of 600%. As shown in Fig. 11(b), the stress starts from a zero value at 26°C (point $A$), reaches its maximum

---

**Table 2**

Model parameters calibrated on experimental orientation curves of Fig. 3(a) and (c), related to materials A and E.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>LDPE</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>MPa</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>$E_0$</td>
<td>MPa</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>$\mu$</td>
<td>K</td>
<td>410</td>
<td>410</td>
</tr>
<tr>
<td>$C_s$</td>
<td>-</td>
<td>8</td>
<td>8.5</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>K</td>
<td>205</td>
<td>205</td>
</tr>
<tr>
<td>$E_i$</td>
<td>MPa</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>$C_v$</td>
<td>MPa</td>
<td>5.434</td>
<td>9.88</td>
</tr>
<tr>
<td>$h_1$</td>
<td>MPa</td>
<td>120</td>
<td>105</td>
</tr>
<tr>
<td>$h_2$</td>
<td>K</td>
<td>2.1</td>
<td>1.5</td>
</tr>
<tr>
<td>$h_3$</td>
<td>MPa</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>219</td>
<td>235</td>
</tr>
</tbody>
</table>

---

Fig. 9. Model response for orientation tests. Comparisons with experimental data on materials A and E.
value (point $B$) and then decreases. As expected from Eq. (9), the stress stabilizes around an asymptotic value at temperatures above $T_m$ (point $C$).

To verify the irreversibility of the retraction process mentioned in Section 3.1.5, we simulate a simple uniaxial tension test, with displacement control and prescribed homogeneous constant temperature field. Fig. 11(c) and (d) shows the results predicted by the model. Upon unloading, at zero stress, we fix the residual strain (point $A$) and we start lowering the temperature. In such a case, the specimen does not change its state (i.e., points $A$ and $B$ present the same values for the stress and residual strain).

Following this line, we simulate the experimental constrained thermal retraction tests on materials A and E for specimens oriented at a temperature of 30 °C and maximum deformation of 600%. Fig. 12(a) shows the comparison between numerical and experimental results. As it can be observed, the predicted stress reaches its maximum value at a temperature lower than the one reached by the experimental stress, and then decreases. The predicted stresses for material A are lower than those
for material E, as experimentally observed. The predicted maximum value matches well the experimental one for material E. Discrepancies, especially in terms of concavities of the curves and temperature ranges, are attributed to the fact that the investigated material manifests a viscoelastic behavior (discussed in Section 5.1), which is not taken into account by the proposed model and influences the real trend of the stress curve. Moreover, the different steps of the experimental setup (see Section 2.2) are simplified during the simulation.

5.3. Free thermal retraction test

Also in such a case (see Section 2.3), we make a similar qualitative interpretation of the test. We simulate such a test as simple uniaxial tension test, with displacement control and prescribed homogeneous constant temperature field. Upon unloading, at zero stress, we fix the stress and we start increasing the temperature until a value above the melting temperature, $T_m$. Fig. 13(a) and (b) shows the qualitative model response for a specimen orientated at a temperature of 26°C and maximum deformation of 600%. As shown in Fig. 13(b), the strain starts from a residual value at 26°C (point A) and then decreases until point B, i.e., a shape recovery takes place by heating.

Following this line, we simulate the experimental tests on materials A and E for specimens oriented at a temperature of 30°C and maximum deformation of 600%. Fig. 12(a) shows the comparison. As it can be observed, the predicted shrinkage for material A are lower than those for material E, as experimentally observed. Discrepancies in terms of concavities of the curves are again attributed to the fact that the investigated material manifests a viscoelastic behavior (discussed in Section 5.1), which is not taken into account by the proposed model and influences the real trend of the curve.

6. Conclusions

The present work has first presented the results of an uniaxial experimental investigation on semi-crystalline SMPs. Experimental data have been analyzed to show the main features of material behavior, in particular related to material orientation and thermal retraction. Then, a simple new one-dimensional finite strain model has been introduced to predict the behavior of LDPE and HDPE polymers, observed experimentally, in a fixed range of temperatures between the glass transition and the melting temperatures, which is the most significant from the industrial point of view. The model has been demonstrated
to be able to describe qualitative aspects of material behavior, involving both orientation and thermal retraction, as well as to predict experimental orientation processes for semi-crystalline PE-based polymers with different densities. The experimental and modeling study of the viscoelastic behavior of the considered polymer will be the object of future work. Moreover, ongoing work will focus on the model extension to include material orientation at temperatures above the melting temperature and to a three-dimensional framework to possibly simulate important industrial processes, e.g., packaging.

Acknowledgment

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Appendix A. Adopted expression for the Young’s modulus

The function \( E = E(T, \chi) \), introduced in Eq. (5), represents the Young’s modulus, which we assume to strongly depend on temperature, \( T \), and on phase, \( \chi \), as reported in Eq. (8). Such an expression has been demonstrated to be the only function of \( \chi \) such that \( d\tau/dc = 0 \), when no hardening is assumed, i.e., when we have a flat plateau in the stress, \( \tau \), versus strain, \( \varepsilon \), diagram during phase transformation; see (Auricchio et al., 2009) for a detailed discussion and proof of the claim.

To prove such a claim in our model, we follow the line of the work by Auricchio et al. (2009) and we start by computing the consistent tangent, \( d\tau/dc = 0 \), in the case \( 0 < \chi < 1 \) and \( F = 0 \). We differentiate Eq. (9) with respect to time, obtaining:

\[
\dot{\tau} = \frac{d\tau}{dc}\dot{\varepsilon} = E\dot{\varepsilon} + \left[ E\left(\varepsilon - \varepsilon^r\right) - E\left(\varepsilon^r\right)\right]\dot{\chi} \tag{A.1}
\]

where \( E' \) and \( (\varepsilon^r) \) represent the derivatives with respect to \( \chi \). To compute the consistent tangent, we evaluate \( \dot{\chi} \) as a function of \( \dot{\varepsilon} \). Under the condition \( 0 < \chi < 1 \), the residual equation related to \( X^m \), reads as:

\[
R = X^m - E(\varepsilon^r)'(\varepsilon - \varepsilon^r) + \frac{1}{2} E'(\varepsilon - \varepsilon^r)^2 = 0 \tag{A.2}
\]

Differentiating with respect to time, we obtain:

\[
\frac{\partial R}{\partial \chi} \dot{\chi} + \frac{\partial R}{\partial \varepsilon} \dot{\varepsilon} = 0 \tag{A.3}
\]

from which:

\[
\dot{\chi} = -\frac{\partial R}{\partial \varepsilon} \left( \frac{\partial R}{\partial \chi} \right)^{-1} \dot{\varepsilon} \tag{A.4}
\]

After some simple computations, we obtain:

\[
\dot{\chi} = -\frac{E(\varepsilon^r)' - E(\varepsilon - \varepsilon^r)}{E(\varepsilon^r)'^2 - 2E(\varepsilon^r)'(\varepsilon - \varepsilon^r) + \frac{1}{2} E'(\varepsilon - \varepsilon^r)^2} \dot{\varepsilon} \tag{A.5}
\]

After substituting into Eq. (A.1), we obtain the expression for the consistent tangent, as follows:

\[
\frac{d\tau}{dc} = E - \frac{\left[ E(\varepsilon^r)' - E(\varepsilon - \varepsilon^r)\right]^2}{E(\varepsilon^r)'^2 - 2E(\varepsilon^r)'(\varepsilon - \varepsilon^r) + \frac{1}{2} E'(\varepsilon - \varepsilon^r)^2} \tag{A.6}
\]

Under the considered conditions, we have a flat response, i.e., \( d\tau/dc = 0 \). Such an assumption, in combination with Eq. (A.6), gives rise to the following equation:

\[
E\left[ E(\varepsilon^r)'^2 - 2E(\varepsilon^r)'(\varepsilon - \varepsilon^r) + \frac{1}{2} E'(\varepsilon - \varepsilon^r)^2\right] = \left[ E(\varepsilon^r)' - E(\varepsilon - \varepsilon^r)\right]^2 \tag{A.7}
\]

which, assuming \( \varepsilon \neq \varepsilon^r \) and simplifying, becomes:

\[
EE'' = 2E(\varepsilon^r)' \tag{A.8}
\]

Hence, by requiring the elastic modulus \( \chi \rightarrow E(\chi) \) to be a function of \( \chi \) only, namely \( E(\chi) = e(\chi) \), this last function \( e \) necessarily fulfills the nonlinear boundary problem (Auricchio et al., 2009):

\[
\begin{cases}
\varepsilon e'' - 2(e')^2 = 0 \quad \text{in} \quad (0, 1) \\
\varepsilon(0) = E_0, \quad e(1) = E_1
\end{cases} \tag{A.9}
\]

Recalling the following Lemma reported in Auricchio et al. (2009), we then prove that expression (8) is the optimal choice for \( E = E(\chi) \).
Lemma. The function $t \rightarrow 1/(\chi/E_1 + (1 - \chi)/E_0)$ is the only classical solution of the nonlinear boundary value problem (A.9).

The reader is referred to the work by Auricchio et al. (2009) for the proof of the above Lemma.

Appendix B. Newton–Raphson method

In Section 4, we state that we employ a Newton–Raphson method to solve the nonlinear problem (36). Accordingly, we need to detail the form of the corresponding tangent matrix.

Linearizing the following equations:

$$
\begin{align*}
Q_1 &= \chi - \chi_n - \Delta \chi \frac{x_{nd} - \frac{\eta}{2}}{\|x_{nd} - \frac{\eta}{2}\|} = 0 \\
Q_2 &= \sqrt{\chi^2 + \Delta \chi^2} + F - \Delta \chi = 0 \\
Q_3 &= \sqrt{\chi^2 + (\gamma^0)^2} + \gamma^0 - \chi = 0 \\
Q_4 &= \sqrt{(\chi - 1)^2 + (\gamma^1)^2} + (\chi - 1) - \gamma^1 = 0
\end{align*}
$$

we obtain:

$$
\begin{align*}
Q_1 &= 1 \\
Q_1, \chi &= -\text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\} \\
Q_1, \phi &= 0 \\
Q_1, \gamma^1 &= 0
\end{align*}
$$

$$
\begin{align*}
Q_2, \chi &= \left(\frac{F}{\sqrt{\chi^2 + \Delta \chi^2}} + 1\right) \left(\text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\} \left(\frac{\partial x_{nd}}{\partial \chi} + \frac{\eta}{2} \frac{\partial \eta}{\partial \chi}\right) - \frac{\partial \eta}{2 \partial \chi}\right) \\
Q_2, \chi &= \frac{\Delta \chi}{\sqrt{\chi^2 + \Delta \chi^2}} - 1 \\
Q_2, \phi &= -\frac{F}{\sqrt{\chi^2 + \Delta \chi^2}} \text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\} - \text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\} \\
Q_2, \gamma^1 &= -\frac{F}{\sqrt{\chi^2 + \Delta \chi^2}} \text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\} - \text{sign}\left\{x_{nd} + \frac{\eta}{2}\right\}
\end{align*}
$$

$$
\begin{align*}
Q_3, \chi &= \frac{\chi}{\sqrt{\chi^2 + (\gamma^0)^2}} - 1 \\
Q_3, \chi &= 0 \\
Q_3, \phi &= \frac{\gamma^0}{\sqrt{\chi^2 + (\gamma^0)^2}} + 1 \\
Q_3, \gamma^1 &= 0
\end{align*}
$$

$$
\begin{align*}
Q_4, \chi &= \frac{\chi - 1}{\sqrt{(\chi - 1)^2 + (\gamma^1)^2}} + 1 \\
Q_4, \chi &= 0 \\
Q_4, \phi &= 0 \\
Q_4, \gamma^1 &= \frac{\gamma^1}{\sqrt{(\chi - 1)^2 + (\gamma^1)^2}} - 1
\end{align*}
$$
with:

\[
\frac{\partial X_{\text{old}}}{\partial \chi} = -E \left( (\varepsilon^{e})' \right)^2 + 2E' (\varepsilon^{e})' (\varepsilon - \varepsilon^{e}) - \frac{1}{2} E'' (\varepsilon - \varepsilon^{e})^2
\]

\[
\frac{\partial \eta}{\partial \chi} = -h_1 \exp \left[ \frac{E_{h_1}}{T - T_0} \right] + 2h_2 \exp \left[ \frac{E_{h_2}}{T - T_0} \right] (1 - \chi) + 3h_3 \exp \left[ \frac{E_{h_3}}{T - T_0} \right] (1 - \chi)^2
\]

\[
E = \exp \left[ \frac{\beta}{T - T_0} (E_1 - E_0) E_0 \right]
\]

\[
E' = 2 \exp \left[ \frac{\beta}{T - T_0} (E_1 - E_0)^2 E_0 \right]
\]

and

\[
(\varepsilon^{e})' = -C_2 \exp \left[ \frac{\alpha}{T - T_0} \right]
\]

Here, subscript comma indicates derivation with respect to the quantity following the comma. For instance, \(Q^1_{\chi}\) indicates the derivation of the first scalar equation \(Q^1\) with respect to \(\chi\).

References


