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An experimental, theoretical and numerical investigation of shape memory polymers

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ABSTRACT

The present paper deals with the experimental analysis, constitutive modeling and numerical simulation of a class of polymers, exhibiting shape memory effects. We first present and discuss the results of an experimental traction-shrinkage campaign on semi-crystalline shape memory polymers, particularly, on low-density and high-density polyethylene-based polymers. Then, we develop a new one-dimensional phenomenological constitutive model, based on the so-called phase transition approach and formulated in a finite strain framework, in order to reproduce experimental observations. The model is treated through a numerical procedure, consisting in the replacement of the classical set of Kuhn–Tucker inequality conditions by the Fischer–Burmeister complementarity function. Numerical predictions reveal that the model is 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 polyethylene-based polymers with different densities.

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).

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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; Atli 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% (Atli 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; Sedlák 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 (Khonakdar 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.