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Micromechanical modelling of reversible and irreversible thermo-mechanical deformation of oriented polyethylene terephthalate

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ABSTRACT

In this article, the reversible and irreversible thermo-mechanical time-dependent deformation of oriented polyethylene terephthalate film is studied. A mean-field model is used to simulate these effects along with the long-term creep behaviour, taking into account the underlying material microstructure and differences in constitutive behaviour of the phases. The material is modelled as an aggregate of layered two-phase domains. Irreversible deformation, or partial shape recovery, results from the presence of an internal stress, which is characterised and incorporated into the constitutive behaviour of the non-crystalline phase. Using the micromechanical approach, the deformation mechanisms at the local scale are analysed.

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1. Introduction

Predictable mechanical response and high dimensional stability are major requirements for polymer substrates used in the production of flexible electronics [1,2]. There are a number of candidates for the substrate material with the most common materials being semicrystalline, oriented and thermally stabilised polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) films. The goal of this work is to predict the dimensional stability of the polymer film at temperatures above the glass transition temperature, i.e. to simulate reversible and irreversible deformation of the film under these industrially relevant conditions based on the underlying microstructural information.

The polymer films studied here are produced by sequential biaxial stretching at temperatures above the glass transition (T_g) and subsequent cooling down to room temperature [3]. Upon heating above T_g these films demonstrate irreversible deformation under stress-free conditions, referred to as thermal shrinkage, or an emergence of shrinkage stress if the dimensions are fixed [4–6]. This process is significantly influenced by the manufacturing conditions [7]. Such behaviour can be classified as a shape-memory effect, where the partial recovery of the original shape is a result of increased molecular mobility above T_g and the driving force is due to the tendency of the structure to increase its entropy by relaxing the oriented conformation [8]. In oriented amorphous PET there is

evidence that the molecular origin of this process lies in a redistribution of the rotational isomers along the polymer chains, leading to their coiling [9].

The modelling approaches of shape-memory polymers can roughly be divided into macroscopic and micromechanical [8,10]. In macroscopic models, the material behaviour is simulated as the behaviour of a system constructed of elastic, viscous and purely plastic elements. In this case, a nonlinear temperature-dependent viscosity captures the shape memory effect. In contrast, micromechanical approaches take into account aspects of the material microstructure, while often lacking some reliable experimental data at that fine scale. In [11], the material was considered to consist of active and frozen phases with the phase transition being described by a temperature dependent volume fraction. A similar approach was used in [12] to construct a large deformation model based on the rules of mixtures. In [13], a model for semicrystalline shape-memory polymers was presented, where the shape-memory effect occurred due to a tendency of each phase to return to its initial configuration.

In this article, the effect of shape recovery of a PET film is modelled using a micromechanical model referred to as the composite inclusion model [14–18]. In this model, the material is considered to consist of two phases: the crystalline and the amorphous phases, out of which layered domains are constructed. Here, the amorphous phase is referred to as non-crystalline since it significantly differs from purely amorphous material due to the constraints induced by crystalline lamellae and the presence of tie molecules. The material behaviour is modelled as the behaviour of an

aggregate of such layered domains. Crystal plasticity [19] is used as a constitutive model for the crystalline phase, with viscous slip on the (limited number of) slip systems. The non-crystalline phase can be modelled with one of the material models suitable for glassy polymers, such as the model by Buckley et al. [20,21], by Boyce et al. [22,23] and by Govaert et al. [24,25]. In this article, the model by Govaert et al., referred to as the EGP model, is used.

In [26], the composite inclusion model was used to describe the deformation kinetics of oriented HDPE. However, the model was found to lack the contribution of the pre-stretched amorphous phase. In [18], this model was used to simulate short-term and long-term behaviour of the oriented PET film taking into account this pre-orientation. In the present article, the constitutive models of the phases are further extended, i.e. thermal expansion is added to the model and a relaxation of the internal pre-stress state of the PET film is incorporated to simulate the behaviour of the film at high temperatures and to model reversible and irreversible thermal deformation. The aim of this article is to simulate these effects based on the underlying microstructure, and therefore to obtain a reliable structure–property relationship and to analyse microstructural deformation processes.

2. Experimental methods

Thermally stabilised oriented polyethylene terephthalate film, manufactured by DuPont Teijin Films, was provided for the experimental analysis. The film is produced by sequential biaxial stretching with draw ratios 3.1 and 3.4 in machine direction (MD) and transverse direction (TD) respectively. The draw temperature in the first (MD) stage was set to 90 °C, and the TD draw temperature was set to 110 °C. The MD stretch stage is at a "constant width", and when heated, the film is accelerated between two rotating rollers which causes the material to stretch to a fixed ratio. The TD draw was performed in a "stenter oven", where each edge of the film was clamped to a continuously moving chain. By causing the path of the two chains to diverge, the edges of the film were continuously drawn apart. The temperature during the final heat set was set to 210 °C. The manufactured film had an average thickness of 125 μm, a width of 90 cm and an approximate crystallinity of 50%.

To measure irreversible deformation of the film resulting from different heating conditions, the behaviour of oriented PET film was measured using two different techniques. Strain measurements at varying temperatures were performed under uniaxial tensile stress-controlled conditions using a Zwick Z010 universal tensile tester equipped with a video extensometer, a temperature controlled chamber and a 1 kN force cell. Samples, with a shape according to ISO 527-2, type 1BA, cut in different directions were heated from 60 °C to 190 °C with subsequent annealing at 190 °C. Three heating rates were imposed: constant rates of 1 °C/min, 5 °C/min and ∼10 °C/min, which is the maximum heating rate of the temperature controlled chamber. Measurements were performed under imposed stress of 0.16 MPa, which is sufficient to keep the sample straight while not leading to noticeable creep effects at high temperatures. Prior to testing, the samples were dried in the temperature controlled chamber at 60 °C for 60 min to prevent interference of dehydration-induced contraction with the measurements. For the samples heated at 10 °C/min and 5 °C/min, multiple measurements were performed to ensure reproducibility.

The residual (i.e. irreversible) deformation after cooling down was measured using digital image correlation (DIC). Dried samples with dimensions of 15 cm by 10 cm (in TD and MD, respectively) with a grid of 16 × 11 dots were placed in a pre-heated oven and annealed for a certain time. Images of samples (with the size of 3300 × 2200 px) were taken before the heat treatment and after removing the sample from the oven and cooling it down to room temperature, thus eliminating reversible thermal deformation (thermal expansion). The two-dimensional strain was extracted from the images by correlating the displacement of the dots across the series of images. A uniform strain field in each sample was assumed, since the strain inhomogeneity within one sample was of the same order of magnitude as the deviation of the average strain within multiple samples tested at identical conditions. The actual calculated strain in each sample tested at certain conditions was averaged from three subsequently taken images. Since heating and annealing of the samples was performed at stress-free conditions, film wrinkling, resulting from inhomogeneity of the sample and of the temperature field, was observed. Therefore, when images of the samples were recorded, the samples were straightened by putting a glass plate on top.

The anisotropy and inhomogeneity of the film was studied in [18]. It was found that for the centre of the film (i.e. the middle position across the width) the principal strain directions correspond to MD and TD and for the sides the principal directions are rotated by 15°. Therefore the effective MD and TD, which are rotated by a small angle, are introduced here for the right part of the film. In [18], the mechanical behaviour along the effective directions was found to be similar across the width of the film. Therefore, here samples from the sides of the film were also used for the experimental programme with strain measurements performed along the effective machine and transverse directions.

To measure the coefficient of thermal expansion (CTE) of isotropic PET, semicrystalline PET samples were prepared from isotropic amorphous PET, which was also supplied by DuPont Teijin Films, by annealing in an oven for 1, 4, 10 and 13 h at 100 °C. Crystallinity of the samples was measured by X-ray diffraction and DSC. To determine the CTE, PET samples were heated from 30 °C to 70 °C and then cooled down to 30 °C at a rate of 5 °C/min. The cycle was repeated 2 times, and the obtained measurements of the CTE during heating and cooling were averaged. The deformation field was obtained by DIC. The observed deformation of the samples was homogeneous and linearly dependent on temperature within the imposed temperature region.

The CTE of the oriented PET film was measured using the same technique as used to measure the CTE of isotropic PET, however during the heating stage of the first cycle, strain was not recorded, and thus only 3 measurements (2 during cooling and 1 during heating) were taken. Measurements on 3 samples from the centre of the film were performed and the results were averaged.

3. Measurements, oriented material

The thermomechanical behaviour of PET film under different conditions was studied. The imposed temperature profile is
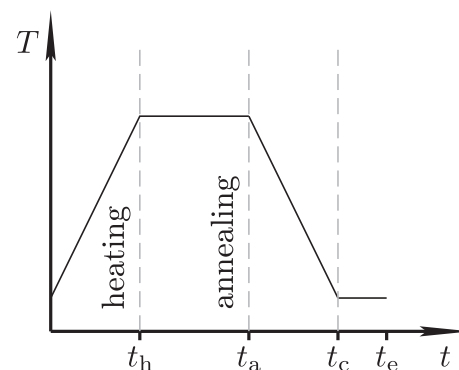

Fig. 1. Schematic representation of the imposed temperature profile.