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Property modelling

## Elongational behavior of amorphous polymers in the vicinity and above the glass transition temperature



Anthony Thévenon, René Fulchiron\*

Ingénierie des Matériaux Polymères (IMP), IMP@LYON1, CNRS-UMR 5223, Université Claude Bernard Lyon 1, 15 Boulevard Latarjet, 69622 Villeurbanne, France

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### ABSTRACT

The understanding of the relationship between morphology and thermomechanical properties of thermoplastic films is a key step to predict their behavior during processing involving large elongational strains. Moreover, the film fabrication process itself (cast mono or bi-stretched, blown film) is responsible for polymer chain orientations which could lead to anisotropic thermomechanical properties. The aim of this work is to study the elongational behavior of amorphous polymer films (PS, PC and PET), depending on temperature and strain rates. Basic modeling parameters (relaxation spectrum) were determined from frequency sweep tests using both melt state rheology and dynamic mechanical analysis. Extensional viscoelastic behavior was studied for temperatures higher than the glass transition temperature. The comparison between experiments and predictions of the Lodge and MSF models exhibits moderate discrepancies, especially for temperatures near  $T_g$ . However, by taking into account the relaxation times characteristic of the glass relaxation, the model predictions are improved. Moreover, based on specially prepared PET films presenting some molecular orientation, it is shown that the pre-orientation can be reasonably taken into account by introducing an equivalent strain history in the prediction of the Lodge model.

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### 1. Introduction

Industrial polymer processing techniques such as thermofforming and overmolding, often involve thermoplastic films submitted to intense and combined stresses (deformation, temperature). Therefore, understanding the relationship between the morphology and the thermomechanical properties of thermoplastic films is a key step to predict their behavior in a processing operation [1,2] where they are generally strained in a mono- or bi-axial elongation mode. Moreover, for predicting the processability of the films, modeling of the thermomechanical behavior must be reliable for a large temperature range, including the vicinity of the glass transition in the case of amorphous polymers (for semi-

crystalline materials, the processing temperature is generally far from  $T_g$ ).

The modeling of the non-linear viscoelastic behavior of polymer melts is still largely discussed in the scientific literature in the framework of differential constitutive equations [3–7], such as Giesekus [8] or Phan-Thien and Tanner [9] models, as well as integral constitutive equations [10–12] such as Lodge rubber-like liquid [13], Doi-Edwards [14] or Molecular Stress Function (MSF) [15] models. Generally, the differential models [16] are built on (1) a relaxation spectrum derived from linear viscoelasticity analysis, (2) an admissible expression of the time derivatives of the rate of strain and stress tensors (convected derivatives) to ensure the model objectivity (independence of the chosen frame) and (3) additional quadratic terms involving the stress and the strain derivative tensors for reducing the stress. This third point can be considered as the way to bring the actual non-linearity into the model.

\* Corresponding author. Tel.: +33 4 72 43 15 67.

E-mail address: [rene.fulchiron@univ-lyon1.fr](mailto:rene.fulchiron@univ-lyon1.fr) (R. Fulchiron).

Without these terms, the model is merely considered quasi-linear. Also, the commonly used integral models [16,17] contain (1) a memory function (based on the relaxation spectrum), (2) a finite strain tensor such as the Cauchy, the Finger or the Doi-Edwards orientation tensors, (3) a damping function, decreasing for increasing strain and reducing the stress. Physically, in the context of polymer network theories, this damping function was introduced to take into account the change of the amount of temporary strands due to the strain. However, in a more recent molecular dynamics approach of Doi and Edwards [14], this function is related to the stress undergone at the molecular level, which is weighted by the variation of the tube diameter [17]. Here again, if the damping function is considered constant and equal to unity, the model can be called quasi-linear.

In all cases, a time dependent function (expressed in terms of relaxation spectrum or memory function) is the starting point of the modeling. This spectrum is derived from linear viscoelastic measurements and, moreover, it comprises all the temperature effects. It can be pointed out that the generally published works on the modeling of non-linear viscoelastic behavior do not address in detail the assessment of the relaxation spectrum, let alone the temperature effect because this is outside the scope. However, as shown further, when taking into account the temperature effect, caution must be observed in determining the relaxation spectrum, all the more so for modeling the behavior at temperatures near  $T_g$ .

In the present paper, the effect of the temperature on the elongational behavior will be discussed by focusing on the relaxation spectrum assessment. Examples will be given for different amorphous polymers: polystyrene, polycarbonate and a polyethylene terephthalate modified with cyclohexanedimethanol to avoid its crystallization.

## 2. Experimental section

### 2.1. Materials

The commercial polystyrene film was 100  $\mu\text{m}$  thick (PS100) obtained by a bi-axial stretching cast process. The melt state zero shear viscosity obtained from dynamic rheological measurements was  $\eta_0 = 7.5 \times 10^4 \text{ Pa s}$  at 180 °C and the number and weight average molar mass obtained by Size Exclusion Chromatography (SEC) were 200 kg/mol and 340 kg/mol, respectively. From differential scanning calorimetry (DSC) measurements, the glass transition was determined to be near 100 °C.

The polycarbonate film was also commercial, obtained by cast-film extrusion and 375  $\mu\text{m}$  thick (PC375). The measured zero shear viscosity of this polymer was  $\eta_0 = 1.6 \times 10^6 \text{ Pa s}$  at 180 °C. From SEC, the number average molar mass was of 36 kg/mol and the weight average molar mass of 47 kg/mol. The glass transition temperature measured by DSC was 150 °C.

The films of modified polyethylene terephthalate were specially prepared by Toray Plastics either in the form of non-oriented cast film 400  $\mu\text{m}$  thick (PET400) or mono-oriented film 100  $\mu\text{m}$  thick (PET100). These films will be helpful to analyze the effect of mono-orientation since this

is the only difference between PET400 and PET100. The measured zero shear viscosity of this PET was  $\eta_0 = 1.78 \times 10^4 \text{ Pa s}$  at 170 °C. The measured glass transition temperature was 75 °C.

### 2.2. Tensile tests

To highlight the possible anisotropic mechanical behavior due to the film fabrication process, tensile tests at ambient temperature were carried out on a MTS QT25 tensile testing machine. Dumbbell-shaped samples were cut parallel and perpendicular to the drawing direction (designated MD and TD, respectively). The extension rate was fixed at 20 mm/min.

### 2.3. Melt rheological measurements

The melt viscoelastic behavior of each material was characterized by frequency sweep measurements using a rotational rheometer (ARES from TA Instruments or SR5 from rheometrics) and a parallel plates geometry (diameter 25 mm and gap  $\sim 1 \text{ mm}$ ). The experimental temperatures ranged from 130 to 200 °C for PS100, from 160 °C to 260 °C for PC375 and from 90 °C to 170 °C for the PET.

### 2.4. Dynamic mechanical analysis measurements

Some experiments were carried out using a dynamic mechanical analyzer (DMA Q800 from TA Inst.) in tension mode between 80 °C and 120 °C for PS100, between 140 °C and 175 °C for PC375 and between 78 °C and 90 °C for the PET.

### 2.5. Elongational rheology

The uni-axial elongational behavior was analyzed using the Extensional Viscosity Fixture [18] (EVF) mounted on the ARES rheometer. This device based on the Meissner concept [19] ensures a constant elongational strain rate to the sample during the experiment. The measurements were performed at different strain rates between 0.1  $\text{s}^{-1}$  and 5  $\text{s}^{-1}$ . For PS100, the measurements temperature ranged from 100 °C to 140 °C, whereas it ranged from 180 to 220 °C for PC375. For the PET, the elongational rheological measurements were carried out only at 90 °C. The samples for these measurements were prepared by cutting strips of the films of 10 mm  $\times$  25 mm and sticking them on the EVF drums.

## 3. Results and discussion

### 3.1. Tensile tests

Figs. 1–3 show the nominal stress-strain curves obtained by stretching in both Machine (MD) and Transverse (TD) directions. For PS100 and PC375, the curves in both directions are very similar, revealing that there is no preferential molecular orientation. Actually, some molecular orientation in the film plane may exist (especially for PS100 because of the thinness) but the similarity of the curves in both directions indicates that this orientation is regularly

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