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A formulation of the cooperative model for the yield stress of amorphous polymers for a wide range of strain rates and temperatures

J. Richeton, S. Ahzi*, L. Daridon, Y. Rémond

Institut de Mécanique des Fluides et des Solides-UMR 7507, Université Louis Pasteur/CNRS, 2 rue Boussingault, Strasbourg 67000, France

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Abstract

The mechanical response of solid amorphous polymers is strongly dependent on the temperature and strain rate. More specifically, the yield stress increases dramatically for the low temperatures as well as for the high strain rates. To describe this behavior, we propose a new formulation of the cooperative model of Fotheringham and Cherry where the final mathematical form of the model is derived according to the strain rate/temperature superposition principle of the yield stress. According to our development, the yield behavior can be correlated to the secondary relaxation and we propose an extension of the model to temperatures above the glass transition temperature. For a wide range of temperatures and strain rates (including the impact strain rates), the predicted compressive yield stresses obtained for the polycarbonate (PC) and the polymethylmethacrylate (PMMA) are in excellent agreement with the experimental data found in the literature.

Keywords: Yield stress; Modeling; Amorphous polymers

1. Introduction

Many molecular theories have been proposed for the prediction of the yield stress of amorphous polymers. These theories consider the yield behavior as a thermally activated process and account for temperature and strain rate effects. One of the first models was the Eyring transition state theory [1] where the fundamental process of yielding consists of the jump of macromolecule segments from one equilibrium position to another. Later, Robertson [2] proposed an approach explaining how a shear stress can induce flow in an amorphous polymer by changing the actual structure of the polymer chain. Argon [3] developed a model that takes into account the intermolecular resistance to shear yielding with the rotation of chain segments generating two kinks in the chain. Other theories are based on the dislocation concept, such as in the work of Bowden and Raha [4] who calculated the thermal energy necessary for the nucleation of a sheared region (dislocation loop) under an applied stress.

Most of the previous models give an acceptable prediction for the yield stress but only on a specific domain of temperatures and/or strain rates [5]. As a matter of fact, the yield stress increases more rapidly at higher strain rates or lower temperatures than it does at lower strain rates or higher temperatures. In accordance with the Ree-Eyring theory of non-Newtonian viscosity [6], many processes may be required to obtain a good description over a wide range of temperatures and strain rates. For many amorphous polymers, Bauwens-Crowet, Bauwens and co-workers [7–12] have shown that generally two rheological processes are necessary for the modeling of the yield stress. The equation resulting from the Ree-Eyring theory involves two activation processes, α and β. It is given by:

$$\frac{\sigma_y}{T} = A_\alpha \cdot \left(\ln(2C_\alpha \dot{\varepsilon}) + \frac{Q_\alpha}{kT} \right) + A_\beta \cdot \sinh^{-1}\left(C_\beta \dot{\varepsilon} \exp\left\{ \frac{Q_\beta}{kT} \right\} \right) \quad (1)$$

where σ_y is the yield stress under uniaxial loading, T is the absolute temperature, k is the Boltzmann constant, $\dot{\varepsilon}$ is the strain rate, $Q_i (i = \alpha, \beta)$ are activation energies for the two processes α and β, and finally A_i and C_i are activation parameters. The process α refers to low strain rates and high

* Corresponding author. Tel.: +33 3902 42952; fax: +33 3886 14300.
E-mail address: ahzi@imfs.u-strasbg.fr (S. Ahzi).

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temperatures, whereas the β process refers to high strain rates and low temperatures. The pressure effect on the yield stress can also be considered in the preceding formulation where it has been shown that hydrostatic pressure increases activation energies [13,14]. Moreover it was shown that the use of two Eyring processes acting in parallel also permits to successfully model the yield stress of semi-crystalline polymers [14]. However, in this later case, it is necessary to consider three distinct activated processes each with its own temperature, strain-rate and pressure dependences. Many authors have tried to link the different yield processes of the Ree-Eyring formulation to molecular motions [9–12,14]. The main difficulty in these attempts is that some of the parameters used in the modeling are non-physical quantities. In particular, the values taken by the activation parameters C_i can rarely be related to a physical process.

Within the past 10 years, it has been shown, for amorphous polymers by Povolo and co-workers [15,16] and for semi-crystalline polymers by Brooks et al. [17], that the two Eyring processes acting in parallel for the description of the yield stress on a wide range of temperatures and strain rates can be substituted with the cooperative model of Fotheringham and Cherry [18,19]. In line with these previous studies, we propose a new formulation of the cooperative model for amorphous polymers with the assumption that yield stress must obey the strain rate/temperature superposition principle of Bauwens-Crowet et al. [7]. This assumption allowed us to clearly identify the temperature and strain rate dependence of the model. In a second part of this work, we propose an extension of the model to the glass transition domain (above the glass transition temperature). To the best of our knowledge, this is the first time that: (1) temperature and strain rate dependencies are demonstrated in a very clear and simple way; (2) the activation energy of the cooperative model for amorphous polymers is identified as the energy of the β relaxation; and (3) the cooperative approach is extended to predict yielding above the glass transition point. For a wide range of strain rates and temperatures, the predicted compressive yield stresses obtained for the polycarbonate (PC) and the polymethylmethacrylate (PMMA) give a good agreement in comparison with the experimental results of the literature. In the discussion part of this paper, we emphasize the physical meaning of the proposed model parameters.

2. The cooperative model

2.1. Background

The cooperative model, also called cooperative jump model or Eyring cooperative model, was originally due to the work of Fotheringham and Cherry [18,19]. Two modifications were granted to the original Eyring equation [1]. First, it is assumed that there exists an internal stress σ_i such that the effective stress σ^* is given by:

$$\sigma^* = \sigma_y - \sigma_i \tag{2}$$

This internal stress is a structural parameter, which depicts the arrangement of defects inherited from past thermal history. It provides a better way of expressing the observed macroscopic properties of polymeric materials. Second, the flow in the polymer will be permitted when several polymer chain segments are moving cooperatively [20]. Such a concept was developed to take into account the significance of activation volume in the yield process. According to Fotheringham and Cherry [18,19], the cooperative movement of chain segments involves the occurrence of n elementary transitions. The resulting strain rate $\dot{\varepsilon}$ is given by:

$$\dot{\varepsilon} = \dot{\varepsilon}^* \sinh^n\left(\frac{\sigma^* V}{2kT}\right) \tag{3}$$

where V is an arbitrary activation volume and $\dot{\varepsilon}^*$ is the characteristic strain rate. To write an expression of the yield stress, we get σ^* from Eq. (2) and according to Eq. (3) we obtain the following form:

$$\frac{\sigma_y}{T} = \frac{\sigma_i}{T} + \frac{2k}{V}\sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^*}\right)^{1/n} \tag{4}$$

In the next paragraphs, by assuming the strain rate/temperature superposition principle [7], we will determine the forms of the internal stress σ_i and the characteristic strain rate $\dot{\varepsilon}^*$.

2.2. Strain rate/temperature superposition principle

As it is classically observed, the mechanical behavior of polymers at low temperatures is comparable to the behavior at high strain rates. An increase in temperature will have the same effect on the yield stress as a decrease in strain rate. These observations originate most likely from the well-known time/temperature superposition principle, which describes the equivalence of time (or frequency, herein assimilated as the strain rate) and temperature. For the yield stress of amorphous polymers, Bauwens-Crowet et al. [7] have established that the Eyring plots (i.e. curves representing the reduced yield stress σ_y/T versus the logarithm of the strain rate $\log \dot{\varepsilon}$ for various temperatures) can be shifted to create a master curve for a reference temperature T_{ref}. To illustrate this, Fig. 1 shows a schematic of the Eyring plots for the reference temperature T_{ref} and for other temperatures. From Fig. 1, we can see that the shifts with respect to the master curve are both horizontal and vertical. The expression of these shifts is given by:

$$\begin{cases} \Delta(\log \dot{\varepsilon}) = \log \dot{\varepsilon}(T_{ref}) - \log \dot{\varepsilon}(T) \\ \Delta\left(\dfrac{\sigma_y}{T}\right) = \dfrac{\sigma_y(T_{ref})}{T_{ref}} - \dfrac{\sigma_y(T)}{T} \end{cases} \tag{5}$$