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# Time-dependent thermomechanical constitutive model for polymers based on network theory: application to thermoplastic polymers

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## Introduction

Polymers are characterized by a rich variety of mechanical properties originating from their complex chains network. To capture such intricate structure properties, a number of polymer constitutive models have been proposed and implemented into finite element codes in an effort to solve complex engineering problems. Recent effort by Billon [1,2] focused on proposing alternative route for constitutive equations to model time-dependent mechanical behavior of polymers. This approach is based on a statistical equivalent network concept modified to account for the effect of microstructure evolution associated to inelastic processes taking place during polymer deformation. The model considers microstructure at a mesoscopic level through internal state variables (ISV) evolving in an equivalent statistical network according to classical physic-chemical approaches. Inelastic phenomena are assumed to result from state variables evolution associated to evolution of the network.

## Objectives and Methodology

In this paper, last model enrichment [3] developed to better account for chains interactions as those involved in dense zones is used. Such approach was successively applied to Polyamide 66, which is a semi-crystalline material. To better analyze the relationships of this concept with crystallinity, Polyethylene terephthalate (PET) was chosen. Indeed, this material can be obtained either in an amorphous or in a semi-crystalline state ruling quenching and annealing protocols without any change in molecular architecture or additives. As crystallization is induced through cold crystallization of amorphous injection molded plaques, one can make processing effects as equivalent as possible for the two states. The experiments included non-monotonic tensile test coupled with synchronized digital image correlation and infrared measurement device for capturing the time and temperature dependence of the material. The overall purpose is to examine the influence of crystalline phase on the evolution of chosen internal state variables. The non-gaussian statistical approach of entangled polymer network developed by Edwards and Vilgis [4] is chosen as equivalent network. Internal variables involved are the density of crosslink defining the network in which entanglements induces an excess of entropy referring to the slip link concept as defined by Ball et al. [5].

Five ISVs were introduced in the model:

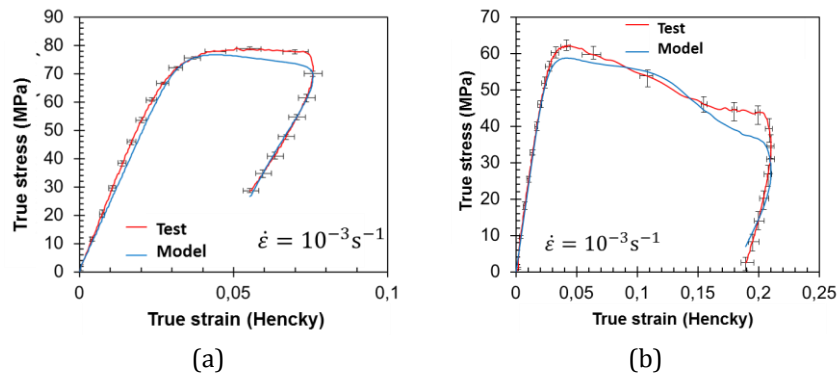
- i)  $\bar{\eta}$  accounts for the degree of mobility of the entanglement points.  $\dot{\bar{\eta}}$  represents the disentanglement of the polymer chain network;
- ii)  $N_s$  represents the density per unit volume of entanglement points.
- iii)  $N_{sc}$  is related weak bonds density (van der Waals or so ever) which acts as crosslinks up to a certain level of energy and then disappears. Those interactions are assumed to be the main ones in dense organized zones such as crystals but not only.  $\dot{N}_{sc}$  represents changes in organization of dense zone due to deformation that is source of inelasticity;
- iv)  $\alpha$  represents the

limit of chain extensibility. The evolution equation of  $\alpha$  depends directly on the density of crosslinks in the polymer chain network; v) Truly permanent node  $N_c$ .

At a mechanical level the modeling approach is equivalent to current methodologies used for continuum mechanics based on thermodynamic constraints with ISVs where they appropriately apply. The thermomechanical deformation of the material follows a multiplicative decomposition  $\mathbf{F} = \mathbf{F}^e \mathbf{F}^i$ , where  $\mathbf{F}^e$  represents the elastic part due to “reversible elastic mechanisms”,  $\mathbf{F}^i$  represents the inelastic part due to the intermolecular interaction between chains inducing a reorganization of the polymer network under deformation.

## Results and analysis

Model succeed in representing the behavior of PET under complex loading at different strain rates whatever it is crystalline or not ( Fig. 1). Other tests such as relaxation were also reproduced.



**Fig. 1** Comparison between model predictions and experiments for (a) tension on a semi-crystalline PET, and (b) tension on an amorphous PET

However ISVs strongly depend on the crystallinity of the material. Permanent nodes are more numerous in crystalline material whereas the entanglements are more active in the amorphous one, which was expected. The connectivity of the network is higher in semi-crystalline PET than in amorphous PET, as expected too. The model tended to show this trend, with slower kinetic evolution of state variables in the semi-crystalline PET compared to the amorphous one.

In conclusion, chosen ISVs and their evolution allow reproducing differences between amorphous and crystalline material. Further work will be to formally relate them to relevant crystalline characteristic

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