On the vertical shift function in the frequency-temperature superposition mastercurves of thermo-rheologically complex polymers: multiaxial constitutive modeling, numerical implementation and experiments

Paolo Iaccarino*†[1,2], Ernesto Di Maio[3], Andrei Constantinescu[4], and Ferdinando Auricchio[5,6]

[1]Scuola Superiore Meridionale – Italy
[2]University of Naples Federico II – Italy
[3]University of Naples "Federico II" – Italy
[4]Institut Polytechnique de Paris – Laboratoire de Mécanique des Solides, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris – France
[5]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Unità di Pavia (INSTM) – via Ferrata 3, 27100 Pavia, Italy
[6]Department of Civil Engineering and Architecture, University of Pavia (UNIPV) – via Ferrata 3, 27100 Pavia, Italy

Abstract

The aim of this work is to define and identify viscoelastic constitutive laws for thermo-rheologically complex polymers, focusing on the open problem of the vertical shift function (alongside the traditional horizontal shift function) in the Frequency-Temperature Superposition (FTS) mastercurves. More precisely, we investigate the feasibility and the interpretability of incorporating a vertical shift function from both theoretical and experimental perspectives, aiming to shed light on the phenomena occurring at the micro-scale. For this study, we have adopted polypropylene, a semi-crystalline and thermo-rheologically complex polymer, as the base material. First, we have experimentally assessed the possibility of producing consistent FTS mastercurves by introducing a vertical shift function using dynamic mechanical tests carried out under various loading scenarios (tensile, shear, torsion). To support these experiments, we have complemented our analysis with calorimetry measurements and with comparisons with available literature data. We found that such vertical shift function seems to have strong physical bases related to structural transitions of the interphase between crystals and the amorphous phase. We then propose a simple multiaxial constitutive model to represent the linear viscoelastic behavior of thermo-rheologically complex polymers. The model is built on a generalized Maxwell framework, explicitly incorporating both vertical and horizontal shift functions. We detail the numerical implementation process (in both the frequency and time domains) and the parameter identification procedure (in

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*Speaker

†Corresponding author: paolo.iaccarino-ssm@unina.it

the frequency domain). Model parameters are hence identified, and the model is validated in the time domain (in creep and stress-relaxation scenarios) comparing the results with experimental data, finding a good qualitative and quantitative agreement. Finally, we provide predictions of the material behavior at various temperatures in the frequency domain. This work could serve as a foundation for the development of nonlinear, physics-based continuum mechanical models for thermo-rheologically complex polymers.