Predicting the rheological behavior of commercial polystyrene melts during isothermal degradation

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Abstract

Several constitutive models have been proposed to describe the viscoelastic behavior of polymer melts. However, most of the reported models do not account for additional chemical processes that may occur with(in) the polymer backbone, such as degradation, ramification or crosslinking. In this work, a time-dependent constitutive model proposed by Marchesini et al. for cement slurries [1], which can describe irreversible effects either of a chemical or physical nature, is for the first time evaluated for polymer melts. This model is based on a single scalar average structural parameter and can describe the evolution of the observed material interactions with time. To evaluate the predictive capability of the model, the isothermal degradation of commercial polystyrene at 250 °C is investigated using both rheological measurements and gel permeation chromatography (GPC). Constant shear rate and oscillatory time sweep tests are performed at different time scales (0 and 240 min) and the flow curves of polystyrene are also obtained [2]. The parameters of the model describing the degradation phenomenon are estimated from both time sweep tests and GPC results. The other parameters of the model are obtained from the flow curves and constant shear rate tests. The model predictions are proved valid to describe such irreversible changes in polymer average structure as well as the viscoelastic behavior of polystyrene melts undergoing degradation.

- [1] F. H. Marchesini, R. M. Oliveira, H. Althoff, and P. R. de Souza Mendes, "Irreversible timedependent rheological behavior of cement slurries: Constitutive model and experiments," J. *Rheol.* 63(2), pp. 247–262, 2019.
- [2] D. V. A. Ceretti; F. H. Marchesini; R. Fiorio; D. R. D'hooge, L. Cardon, *Macromolecules*, in preparation