

Title: Use of non-linear viscoelastic properties to characterize the polyethylene long chain branching topology

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Abstract:

Polyethylene (PE) may have a complex molecular structure, even while only one monomeric unit (ethylene) is present. One crucial factor that increases the structural and topological complexity of the macromolecules composing this materials is the incorporation of comonomers, and the existence of intra- and intermolecular chain transfer reactions during the synthesis, leading to the formation of short chain (SCB) and long chain (LCB) branching [1]. From all the PE family, low density polyethylene (LDPE) presents the most remarkable molecular architecture, combining the presence of both SCB and LCB. The presence of LCB affects not only the linear viscoelastic response (LVR), but also the non-linear (NLVR) properties. LCB leads to further interesting features due to the increased connectivity of the chain network, increasing the rate of disentanglement in shear, but reducing it when an extensional field is applied leading to the typical strain hardening. The relationship between properties and molecular architecture in polymers has been the subject of study along the years, leading to the development of a theoretical framework explaining both LVR and NLVR to a great extent. For this study, a model based on reptation concepts has been chosen, as it can be used with any selected molecular architecture [2]. The theory has been applied to experimental results obtained for a collection of PEs synthesised *via* heterogeneous metallocene catalysts (mPE) supported on a porous carrier leading to a multi-site reaction [3]. The LVR has been studied using both small angle oscillatory shear (SAOS) and creep experiments. Meanwhile, start-up stress growth shear and uniaxial extensional measurements have been used to obtain the NLVR. The complete rheological characterization was used in conjunction with the theoretical model in order to ascertain the molecular topology of the materials. A strong asymmetry in the LCB distribution was predicted in some samples, leading to a characteristic non-linear viscoelastic fingerprint. In Figure 1 typical HDPE (left) and LDPE (right) samples are compared with mPE (centre), showing the strong strain-hardening of the samples studied as well as the shift of this behaviour towards lower extensional strain rates in the case of mPE sample, indicating differences in LCB distribution. The ability to combine an in-depth rheological characterization with molecular computational models is a powerful tool for the exhaustive study of complex polymeric topologies, paving the way for the design of novel material architectures.

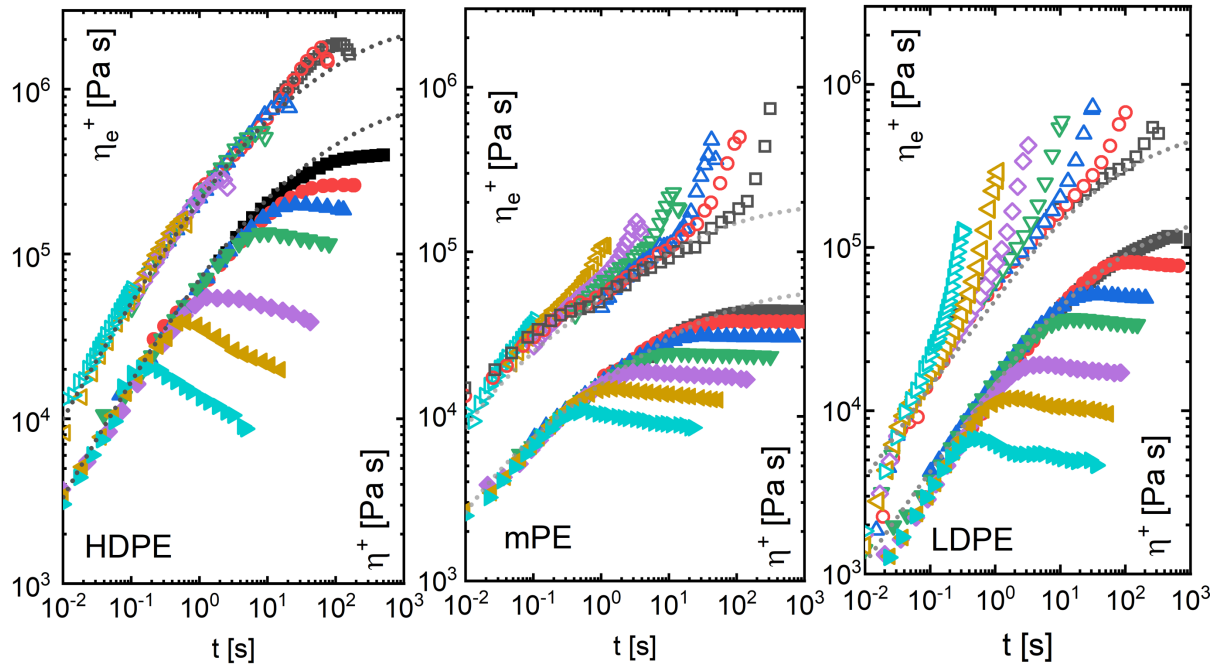


Figure 1. Extensional (open symbols) and shear viscosity (close symbols) at different rates (from 0.01 to 10 s^{-1}) in different polyethylene samples at $150 \text{ }^\circ\text{C}$.