

Nonlinear viscoelastic response of branched polymers and associating polymers for rubber industry

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Rheological properties of polymers for elastomer applications are strongly dependent on their molecular structure and are typically very different from polymers for plastics applications (e.g. PS, HDPE, LDPE). Polymers for elastomer applications show much stronger elasticity and longer relaxation time at their processing temperature. Most commercially available polymers for elastomer applications are entangled polydisperse and branched with an unknown molecular structure. From the experimental point of view, rheological measurements can be carried out in the linear and nonlinear viscoelastic regimes. Both types of measurements can be very fruitful in characterizing polymeric materials and, if combined, they can disclose peculiar physical properties providing a deep insight into molecular structure. That is because the two regimes deal with very different aspects of molecular dynamics. As in the literature the linear viscoelastic regime is widely explored, in this seminar we choose to focus on nonlinear rheological measurements for a number of elastomers, i.e., Polybutadiene (BR), styrene-butadiene copolymers (SBR) and nitrile butadiene (NBR) rubber, which differ significantly in branching content.

The nonlinear viscoelastic response of branched polymers is tested, in this work, with shear and extensional flow startup experiments. Shear flow startup experiments performed on high molar mass randomly branched polymers showed the presence of multiple stress overshoots. The latter were not observed instead for high molar mass linear and star polymers. The phenomenology was assessed also in terms of recovery after the shear flow. Predictions of a model developed within the frame of the “tube” concept (Coppola et al., *Journal of Rheology*, 2014), are shown to be in excellent qualitative and even semi-quantitative agreement with experimental results. Furthermore, recent similar experimental results obtained in large amplitude shear flow with associating polymers are also shown.

Extensional flow startup was performed on polymers with random long chain branching. Taking advantage of an original and simple experimental setup, we were able to investigate the rheological response up to very high Hencky strain, larger than 3.4, which is the usual upper bound of experiments done with Sentmanat Extensional Rheometer. In this way, we were able to discriminate between polybutadienes possessing even just slightly different branching patterns.