Creep Measurements Confirm Steady State in Extension of Highly Branched Polymer Melts

Nicolas J. Alvarez, Jose Manuel Roman Marin, Qian Huang and Ole Hassager

Danish Polymer Center – Department of Chemical and Biochemical Engineering
Technical University of Denmark, Lyngby, Denmark

ABSTRACT

The presence of a stress maximum followed by steady flow in uniaxial extension was first reported by Rasmussen and co-workers for long branched polymers [1]. The measurements were carried out on a filament stretching rheometer (FSR) operating at a constant rate of deformation for a commercial low density polyethylene (Lupolen 3020D). Typically, Hencky strains larger than four are required to establish a steady tensile stress. However in many extensional flow devices, sample inhomogeneity will prevent control of the kinematics at approximately the same Hencky strain, such that a steady flow cannot be observed. Therefore, the validity of the observations of Rasmussen has been a subject of debate. In this work, we have adapted for the first time a FSR to operate in constant stress (creep) mode. Since creep is very effective at obtaining steady flow, we have applied the creep protocol to Lupolen 3020D in order to confirm the steady state measured in constant rate of deformation. The novel creep measurements presented here definitively support previous observations of a stress maximum and confirm the steady state measured previously by Rasmussen et al [1].

INTRODUCTION

One of the great challenges in polymer physics is predicting the viscoelastic properties of branched polymer melts from their molecular architecture. One outstanding problem is a lack of consensus on the existence of a maximum in stress over strain rate as a function of strain prior to reaching a steady state for highly branched polymers. Some groups have even challenged the existence of steady extensional flow for such polymers.

Here, we report observations of transient extensional flow under both constant strain rate and constant stress (creep) deformations using a filament stretching rheometer (FSR). Furthermore, the creep protocol also allows the measurement of the ultimate steady extensional viscosity. The uniqueness of the steady extensional viscosity independent of the start-up protocol is apparently not a settled matter[2]. The creep protocol is validated by comparisons to the linear viscoelastic (LVE) regime.

FILAMENT STRETCHING RHEOMETER

The filament stretching rheometer was first developed by Mckinley and Sridhar for the extension of polymer solutions. Bach et al. developed the first FSR designed specifically for polymer melts, denoted as the DTU-FSR. Fig. 1 shows a sketch of the working principle of the DTU-FSR. Historically, the FSR is operated in constant strain rate mode. The DTU-FSR is the only version with an in-situ control scheme for active control of the filament diameter. The

control scheme works via a feed-forward term and a feedback controller with proportional and integral gain. We have extended the control scheme to allow for the DTU-FSR to operate in constant stress mode [3,4]. This represents the first adaptation of a FSR-device to operate in controlled stress mode [4].

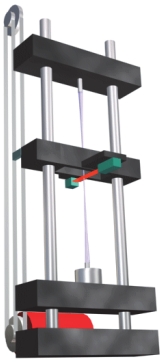

Figure 1. Schematic showing the working principle of the DTU-FSR.

RESULTS

Fig. 2 shows compliance (strain/stress) as a function of time for six different applied stresses. The two lowest stresses follow the prediction of the LVE. In the nonlinear regime, denoted by departure of the compliance from the LVE, LDPE is less compliant, i.e. strain hardening.

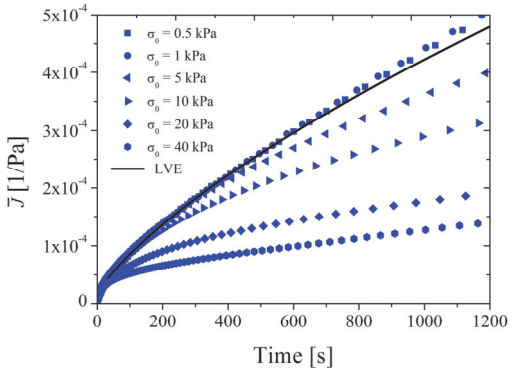

Figure 2. Compliance as a function of time for six applied stresses. The solid line represents the prediction from LVE.

Fig. 3 shows stress over strain rate for both constant stress and constant strain rate deformations. Surprisingly, regardless of the kinematics the transient stress over strain rate goes through a maximum before reaching a constant value. Note that there is no *a priori* reason to expect the two ratios to be the same, since they represent two different deformation histories. Both constant stress and constant strain rate deformations reach the same steady state values.

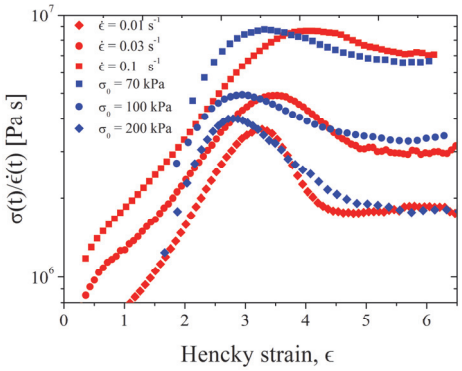

Figure 3. Stress over strain rate as a function of Hencky strain for constant stress and constant strain rate deformations.

CONCLUSIONS

Although the molecular origin of the stress maximum is unknown, it is evident that a steady state cannot be obtained in its absence when far from the LVE. We speculate that the stress maximum signifies a transition to a highly non-linear dynamical state that is outside the applicable range of our current framework for the dynamics of entangled polymeric systems.

ACKNOWLEDGMENTS

The work has been supported the Danish Council of Independent Research, Technology and Production Sciences.

REFERENCES

1. Rasmussen et al. J. Rheol. 49, 369-381 (2005)
2. H. Munstedt et al., Rheol. Acta 37, 21 (1998).
3. Marin et al. JNNFM, 194, 14-22, 2013
4. Alvarez et al. PRL, Mar. 2013