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Note: Method for overcoming ductile failure in Münstedt-type extensional rheometers

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Synopsis

The purpose of this note is to introduce an experimental technique to overcome ductile failure in uniaxial extensional flow and show a simple illustration of its effectiveness. Ductile failure prevents the rheological measurement of transient stress growth at higher strains for certain strain-hardening materials. This reduces the accuracy of nonlinear parameters for constitutive equations fit from transient stress growth data, as well as their effectiveness in modeling extensionally driven processes such as film casting. We propose an experimental technique to overcome ductile failure called encapsulation in which the material that undergoes ductile failure is surrounded by a resin that readily deforms homogeneously at higher strains. The materials are arranged in concentric cylinders and are deformed in parallel. A simple parallel model is shown to calculate the viscosity of the core material and is tested for its robustness in a linear low-density polyethylene/low-density polyethylene system in which the viscosities of each resin are known at all strains, strain rates, and temperatures investigated. Agreement is found at each strain rate investigated across all strains studied. The method is then extended to measure the viscosity of a sparsely branched high-density polyethylene (HDPE) system that undergoes ductile failure at higher strain rates. The technique shows good agreement with experimental results up to the onset of ductile failure in the pure resin and predicts viscosity growth of the HDPE resin well beyond the critical strain for the onset of failure seen in experimental measurements of the pure HDPE. Repeatability of the technique is also illustrated.
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I. INTRODUCTION

Ductile failure, or "necking," in uniaxial extensional flow can prevent the measurement of transient stress growth at high strains for certain polymers. While techniques have been implemented using the filament stretching rheometer (FSR) to control and the Rheometric Scientific RME to delay ductile failure in the extension of melts, these methods themselves are not without flaws. Filaments stretched under controlled deformation on the FSR can still undergo ductile failure at higher extension rates [Bach *et al.* (2003)]. Excessive strain hardening has been recorded for linear low-density polyethylene (LLDPE) melts using the RME [Schulze *et al.* 2001]. Even if these challenges can be overcome, the RME and FSR rheometers are not common to all rheological laboratories. It is, therefore, of interest to explore a technique applicable to a Münstedt-type elongational rheometer (but possibly other designs also) that can delay or control ductile failure.

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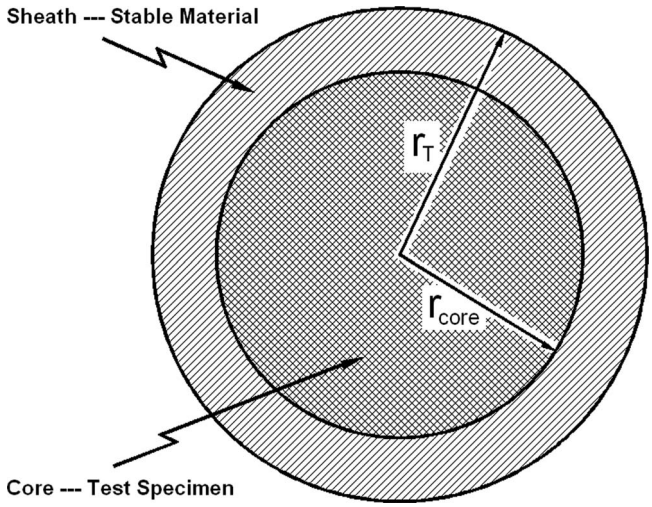

FIG. 1. A cross-sectional diagram of the encapsulated extensional sample. Note that this point of view is on the r, θ plane of the cylindrical sample, with the z axis extending into and out of the page.

In our present work we are particularly interested in the extensional behavior of polymeric resins with sparse long chain branching (LCB) in which extensional data at high strains are needed to interpret the branching architecture in the framework of certain molecular constitutive models. These materials exhibit ductile failure at Hencky strains ($\varepsilon \equiv \dot{\varepsilon}_0 t$) on the order of 1.0 at extension rates on the order of 1.0 s^{-1}. Various studies on predicting the onset of necking have been presented in the literature, most notably by McKinley and Hassager (1999), Joshi and Denn (2003, 2004), and Yao *et al.* (1998, 2000). In this work we introduce an experimental technique to overcome ductile failure in Münstedt-type elongational rheometers in which we encapsulate the material that undergoes ductile failure by a resin that readily deforms homogeneously at higher strains. The encapsulation technique is first shown to measure the transient extensional viscosity data of a core specimen that is in agreement with the extensional viscosity data available from the previous work of Doerpinghaus and Baird (2002, 2003). The encapsulation technique is then applied to a resin that would traditionally undergo ductile failure at the measured strain rate. Application of the encapsulation technique allows for the measurement of transient extensional viscosity of the core material to the strain limitations of the Münstedt-type elongational rheometer used in this study. This achieved strain is higher than that of both the onset of the failure strain and the rupture strain traditionally observed.

II. PROCEDURE

In Fig. 1, illustrated is the approach in which the material of interest (the material that undergoes ductile failure) is encapsulated in a sheath of material with a similar magnitude of shear viscosity. This sheath material is selected on the basis of two criteria. First, that the resin itself readily undergoes homogeneous deformation at all strain rates, strains, and temperatures investigated. Second, the sheath is selected such that it does not significantly strain-harden in order to prevent its response from damping the behavior of the core. Assuming the two materials deform homogeneously in a parallel fashion, the stress in the composite sample is assumed to be the sum of the two components. Thereby

TABLE I. Relevant material characteristics of the polyethylenes used. Properties for Dow Affinity and Equistar resins are from Doerpinghaus and Baird (2002, 2003), and for the HDB3 resin from Wood-Adams and Dealy (2000).

Resin	M_w	M_w/M_N	LCB/10^4 C
Dow Affinity PL 1880	115.800	2.12	0.18[a]
Dow Affinity PL 1840	87 400	2.43	0.57[a]
Equistar NA952	235 500	17.1	39[b]
HDB3	85 700	2.0	0.42[a]

[a]As determined from GPC-LALLS.
[b]As determined from NMR.

knowing the extensional behavior of the sheath and measuring the extensional viscosity of the composite, one can calculate the extensional viscosity of the core according to the following equation:

$$\eta^+_{E,\text{core}}(t) = \frac{\eta^+_{E,\text{composite}}(t) + [x_{\text{core}} - 1]^* \eta^+_{E,\text{sheath}}(t)}{x_{\text{core}}}, \tag{1}$$

where x_{core} is the volume fraction of the core in the encapsulated sample and $\eta^+_{E,i}(t)$ is the transient extensional viscosity of the core, sheath, or composite material.

Three commercially available resins and one industrial model resin (HDB3) are used in this study. Relevant material properties are given in Table I. The two Dow Affinity resins are metallocene-catalyzed, sparsely branched LLDPEs. The branching contents of Affinity PL 1840 and Affinity PL 1880 are 0.57 and 0.18 LCB per 10^4 carbons, respectively [Doerpinghaus and Baird (2002, 2003)]. NA952 is a conventional low-density polyethylene (LDPE) manufactured by Equistar. The Affinity LLDPEs and NA952 LDPE resins readily deform to Hencky strains of at least 3.0 (which is the limit of the Münstedt-type extensional device used here) at all strain rates and temperatures investigated, and their transient uniaxial extensional viscosities at these conditions, as well as the linear viscoelastic response, have been measured previously by Doerpinghaus and Baird (2002, 2003). HDB3 is a metallocene-catalyzed, sparsely branched HDPE resin donated by the Dow Chemical Co. with LCB content of 0.42 LCB/10^4 C [Wood-Adams *et al.* (2000)]. This material undergoes ductile failure at $\dot{\varepsilon}_0 > 1.0\ \text{s}^{-1}$ at Hencky strains lower than the experimental limit of the Münstedt-type extensional rheometer used in this study.

Transient uniaxial extensional measurements are performed using a Rheometrics Extensional Rheometer, Model 9000 (RER-9000), based on the rod-pulling design put forth by Münstedt (1979). The maximum Hencky strain achieved is 3.0 using test specimens that were 22 mm in length prior to extension. Cylindrical samples are compression molded at 5000 psi and 175 °C and then are allowed to cool slowly under atmospheric pressure to eliminate any residual stresses. The samples are then bonded to test clips using Chem Grip-HT Epoxy and then mounted to the RER-9000. For encapsulated samples, the above molding process is done in the same fashion for the sheath material, but before adhesion to the test clip, 50% of the material is drilled out from the center (along the z axis) using a drill press. The center is then filled with the desired test polymer (core specimen) and bonded to test clips. The samples are then immersed in a neutrally buoyant silicone oil bath at the test temperature. After reaching thermal equilibrium, the samples are deformed at the desired extension rate, and the resulting tensile force is monitored using a leaf spring-LVDT (linear variable differential transducer) assembly.

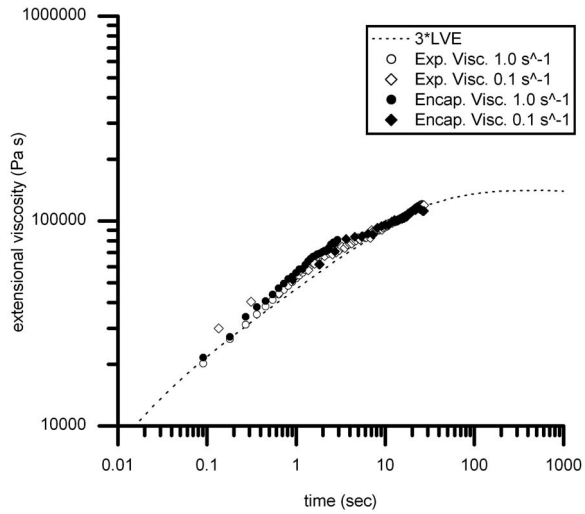

FIG. 2. Transient uniaxial viscosity of pure unencapsulated Affinity PL1880 at $\dot{\varepsilon}_0=0.1\ s^{-1}$ (◇) and $1.0\ s^{-1}$ (○) at 150 °C [Doerpinghaus and Baird (2002)]. Transient uniaxial viscosity of Affinity PL1880 determined from encapsulation using Eq. (1) is shown for $\dot{\varepsilon}_0=0.1\ s^{-1}$ (◆) and $1.0\ s^{-1}$ (●) at 150 °C. The dashed line represents the predicted extensional linear viscoelastic stress growth defined by three times the linear viscoelastic stress growth from simple shear.

Linear viscoelasticity is measured using small-strain dynamic oscillatory shear measurements made on a Rheometrics RMS-800 using a 25 mm cone-and-plate fixture with a 0.1 rad cone angle.

III. RESULTS AND DISCUSSION

A. Encapsulation of a LLDPE that does not undergo ductile failure

The robustness of the encapsulation technique is tested using a system of two resins with known transient extensional viscosity profiles. Measurements are taken at 150 °C with $\dot{\varepsilon}_0=0.1$ and $1.0\ s^{-1}$ using Affinity PL 1880 (LLDPE) as the core material and NA952 (LDPE) as the sheath material. Figure 2 compares the viscosity of Affinity PL 1880 determined using encapsulation and Eq. (1) to that of the data from Doerpinghaus and Baird (2002, 2003). Also shown for comparison in Fig. 2 is the linear viscoelastic envelope measured by Doerpinghaus and Baird (2002) using small-amplitude oscillatory shear. Good agreement between the two sets of viscosities is found across all strains and strain rates with the maximum deviation from experimental values being $<10\%$. These experimental results show that the method of encapsulation could quantitatively lead to the determination of the transient extensional viscosity of a core of LLDPE, suggesting that it is worth extending to a material that undergoes ductile failure.

B. Encapsulation of a HDPE that undergoes ductile failure

HDB3 deformed in uniaxial extension at 170 °C undergoes homogeneous deformation at strain rates of 0.03, 0.1, and 0.3 as shown in Fig. 3. This is checked physically by simple inspection of the sample for homogeneous deformation after elongation. However, HDB3 that is deformed at 170 °C and $\dot{\varepsilon}_0=1.0\ s^{-1}$ undergoes ductile failure at 1.0 unit of Hencky strain before ultimately rupturing at a strain equal to 2.1. This is seen physically during testing by an onset of nonhomogeneous extension, followed by the rupture of the

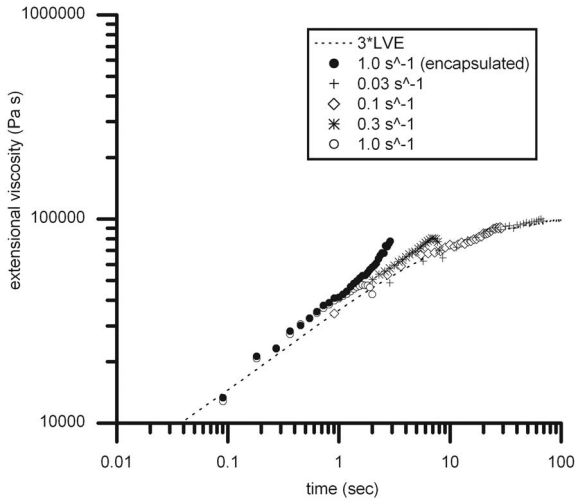

FIG. 3. Transient uniaxial viscosity of pure unencapsulated HDB3 at $\dot{\varepsilon}_0 = 1.0\ s^{-1}$ (○), $0.3\ s^{-1}$ (∗), $0.1\ s^{-1}$ (◇), and $0.03\ s^{-1}$ (+) at 170 °C. Transient uniaxial viscosity of HDB3 determined using encapsulation, and Eq. (1) is shown for $\dot{\varepsilon}_0 = 1.0\ s^{-1}$ (●) at 170 °C. The dashed line represents the predicted extensional linear viscoelastic stress growth defined by three times the linear viscoelastic stress growth from simple shear.

sample into two discrete pieces. The results of this necking are shown graphically in Fig. 3 by the "kneecap" shape in the open circle symbol set of data that resides at strains larger than 1.0.

Application of the encapsulation technique allowed for the measurement of viscosity at strains higher than that at both the onset of the failure strain and the rupture strain. HDB3 is encapsulated in Affinity PL 1840. The extensional viscosity of pure Affinity PL 1840 deformed at $\dot{\varepsilon}_0 = 1.0\ s^{-1}$ and 170 °C is given in Fig. 4. Repeatability of the data is

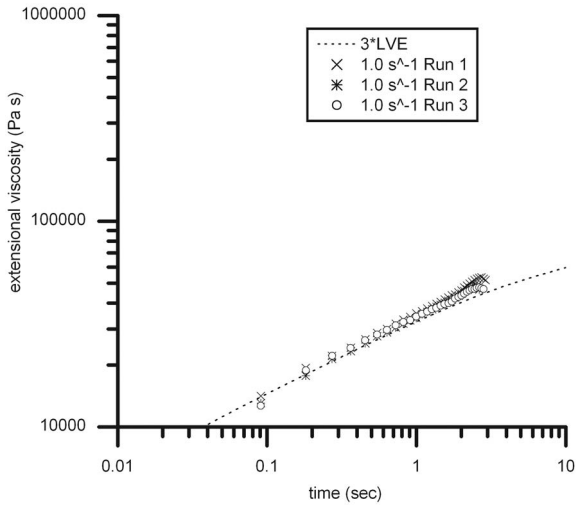

FIG. 4. Illustration of reproducibility and scattering for the transient uniaxial viscosity of Affinity PL 1840 at $\dot{\varepsilon}_0 = 1.0\ s^{-1}$ (○, +, ◇, and ∗). All measurements taken at 170 °C. The dashed line represents the predicted extensional linear viscoelastic stress growth defined by three times the linear viscoelastic stress growth from simple shear.

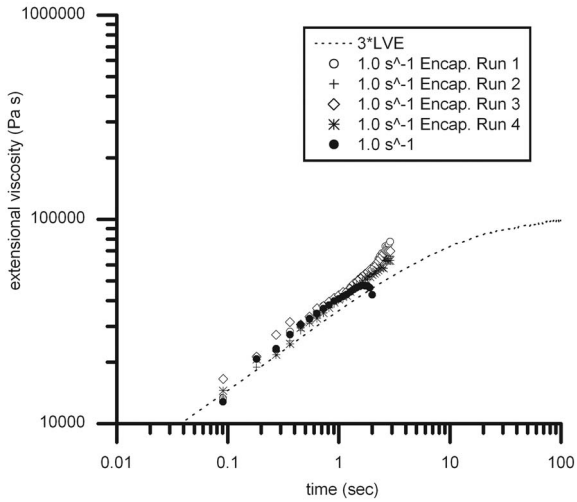

FIG. 5. Illustration of reproducibility and scattering for the transient uniaxial viscosity of HDB3 determined using encapsulation and Eq. (1) elongated at $\dot{\varepsilon}_0=1.0\ s^{-1}$ (○, +, ◇, and ∗). Transient uniaxial viscosity of pure unencapsulated HDB3 at $\dot{\varepsilon}_0=1.0\ s^{-1}$ (●) that undergoes ductile failure is shown for comparison. All measurements taken at 170 °C. The dashed line represents the predicted extensional linear viscoelastic stress growth defined by three times the linear viscoelastic stress growth from simple shear.

also given, with a maximum deviation on the order of 19%. The dark circle symbols in Fig. 3 show the transient extensional viscosity calculated using Eq. (1) in tandem with the data obtained for the encapsulated sample. Excellent agreement is seen at strains less than the strain for the onset of ductile failure. Beyond the traditional failure strain boundary, the viscosity calculated from encapsulation shows continued stress growth. Data are obtained for an additional two units of strains before reaching the experimental limits of the apparatus. Repeatability of the method is illustrated in Fig. 5, with a maximum scattering of the data on the order of 23%. The agreement of the encapsulated data with pure unencapsulated experimental data at strains prior to failure coupled with continuity of the slope of the continuing predicted viscosity curve suggests merit in the predicted viscosity at higher strains.

IV. FUTURE WORK

Encapsulation appears to be a viable experimental technique to gather transient extensional viscosity at strains higher than the onset of ductile failure strain in Münstedt-type extensional rheometers. The ability to increase the range of transient viscosity data available at a given strain could lead to improvements in the quality of the parameters associated with constitutive equations that attempt to model the rheology of branched polymer systems. Future publications of this technique that include more results, theory for stability, and extension to the SER testing platform are currently being investigated by the authors.

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