Extension induced phase separation and crystallization in semidilute solutions of ultra high molecular weight polyethylene

Sara Lindeblad Wingstrand [a], Luna Imperiali [b], Roman Stepanyan [b], Ole Hassager [a, *]

[a] Technical University of Denmark, Department of Chemical and Biochemcial Engineering, Danish Polymer Center, DK-2800, Kgs. Lyngby, Denmark
[b] DSM Research Performance Materials, Materials Science Center, NL-6160BB Geleen, The Netherlands

ARTICLE INFO

ABSTRACT

We investigate the influence of controlled uniaxial extension on various flow induced phenomena in semidilute solutions of ultra high molecular weight polyethylene. Concentrations range from 9 w% to 29 w% and the choice of solvent is paraffin oil. The start-up extensional behavior is measured at various Hencky strain rates $\dot{\varepsilon}$ and at two different temperatures (150 °C and 170 °C) well above the melting point. For Hencky strains $\varepsilon > 0.9$ the qualitative behavior of the samples differ significantly depending on the imposed conditions and the concentration of the samples. Overall we propose two flow scenarios: Scenario 1 - flow induced phase separation resulting in an unstable bulky filament and Scenario 2 - flow induced phase separation and crystallization resulting in a stable deformation and a smooth strongly strain hardening filament. Scenario 2 is observed only at 150 °C at high $\dot{\varepsilon}$ and high concentrations. Scenario 1, observed at both temperatures, is most pronounced at low rates and/or high concentrations.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Ultra high modulus polyethylene fibers are spun from solutions of ultra high molecular weight polyethylene (UHMwPE) [1]. To a large extent fiber spinning processes comprise uniaxial extensional upon extrusion and drawing of the polymeric liquid. The process-ability of UHMwPE solutions is thus determined by the rheological characteristics primarily in extension, yet controlled rheological studies of PE solutions have been performed only in shear flow [2].

In shear, UHMwPE solutions exhibit significant nonlinear characteristics [3]. The long chains are easily deformed by flow causing the solutions to be highly shear thinning. Several studies on UHMwPE solutions utilize paraffin oil (PO) as solvent. It is a convenient solvent due to its low volatility and the fact that the chemical composition is the same as that of UHMwPE. Extensive work on UHMwPE/PO solutions in shear have been performed by Murase and co-workers [4–7]. Apart from significant shear thinning they discovered other highly nonlinear phenomena in these systems. They found that multiple states of heterogeneities can be initiated by flow under the right conditions. At high shear rates the UHMwPE/PO solutions experience concentration fluctuations that

eventually develop into actual phase separation [4]. In addition, at temperatures close to the melting point T_m, the UHMwPE rich phase crystallizes into highly oriented structures [5,6]. These flow induced phenomena have been found to play a huge role in the structural development of UHMwPE fibers during processing [7] as well as the final fiber strength [8,9]. Unfortunately, the deformation in a spin-line is ill defined and lacks control of the deformation. As a result, the imposed deformation is quantified in terms of take-up speed or other measures related to the instrument rather than local deformation of the material. Due to experimental challenges regarding both control of the deformation and the non-stick nature of the sample, studies on polyethylene solutions in controlled extensional flows have, to our knowledge, never been performed.

The purpose of the present study is to characterize solutions of UHMwPE in controlled uniaxial extension. The solvent is PO and the samples are measured at constant deformation rates at temperatures well above T_m. Extension of these non-sticky samples are performed using a filament stretch rheometer (FSR) with a modified sample plate design to prevent slip off. Conditions under which flow induced phase separation and flow induced crystallization (FIC) occur are identified using simultaneous high-speed imaging. We map the regimes under which the different flow induced phenomena occur with respect to imposed deformation rate, polymer concentration, and temperature.

* Corresponding author.
    E-mail address: oh@kt.dtu.dk (O. Hassager).

2. Materials and method

UHMwPE with $M_w = 3\,500\,000\,g/mol$ and a broad molar mass distribution, supplied by DSM and paraffin oil (containing 0.2 w% antioxidant: 2,6-di-tert-butyl-p-cresol) were mixed in an extruder at a temperature well above the melting temperature. Three solutions were prepared containing 5 w%, 10 w% and 20 w% UHMwPE. The solutions were extruded directly into a mould and moulded into discs of diameter $D_0 = 8$ mm and height $h_0 = 6$mm.

Upon cooling to room temperature, some solvent was expelled from the sample due to crystallization of the UHMwPE. Hence, before starting rheological characterizations, the concentration of polymer in the remaining gel samples was determined using TGA (Discovery TGA from TA Instruments). Concentrations were determined from the integrals under the clearly separated PO and UHMwPE peaks (see Supplemental Material for details). The melting point was determined by DSC with an auto sampler from TA instruments (Discovery DSC from TA instruments). In Table 1 specifications regarding polymer concentration obtained from TGA and nominal melting temperature T_m obtained from DSC are given. Table 1 also presents the average number of entanglements Z and the Flory-Huggins predicted equilibrium melting point. The number of entanglements is given by $Z = (M_w/M_e)\phi^\alpha$ where the molar mass between entanglements $M_e = 1120$ g/mol [10] (Note here we assume a dilution exponent $\alpha = 1$). T_m predicted by Flory-Huggins is given by [11].

$$\frac{1}{T_m} - \frac{1}{T_m^0} \cong \frac{R}{\Delta H_f}\left[(1-\phi) - \chi\left(1-\phi^2\right)\right] \tag{1}$$

The equilibrium melting point of the bulk polymer T_m^0 is set to 145 °C and $\Delta H_f = 3900$ kJ/mol is the heat of fusion [5]. The interaction parameter χ is set to 0 as the chemical composition of PE and PO is the same.

Melting temperatures measured by DSC are higher than predicted by Eq. (1). This difference is expected as melting of the PE crystals during the DSC heating ramp does not take place instantaneously. Kinetic delay pushes the melting to higher temperatures in the DSC and thus it tends to overestimate the T_m.

2.1. Small angle oscillatory shear (SAOS)

The linear rheology of the solutions was measured in SAOS. An ARES G2 rheometer from TA Instruments was used with a 25 mm plate-plate geometry. To prevent degradation of the sample, measurements where carried out in the presence of nitrogen. The samples were heated to 170 °C and left to relax. Frequency spectra were collected for $T = 150$ °C and 170 °C. At higher temperatures the loss of solvent was so significant that the rheology no longer was reproducible. Frequency sweeps obtained at different temperatures were shifted and combined into one master curve for each sample.

2.2. Combined filament stretch rheometry and high-speed imaging of non-sticky samples

Extensional rheometry was carried out on a VADER 1000 filament stretch rheometer (FSR) from Rheofilament. The advantage of the FSR is that is allows for controlled deformation to large Hencky strains $\varepsilon > 7$ via a feed back loop [12].

The FSR comprises a moving top plate and a stationary bottom plate between which the sample is sandwiched. Upon movement of the top plate, the fluid is extended uniaxially due to the no slip boundary condition on the plates [13]. The deformation is measured in the mid-filament plane using a laser micrometer and the response of the fluid is monitored via a force cell mounted on the bottom plate. The measure for deformation and response of the fluid is Hencky strain ε and first normal stress difference $\sigma_{zz} - \sigma_{rr}$, respectively:
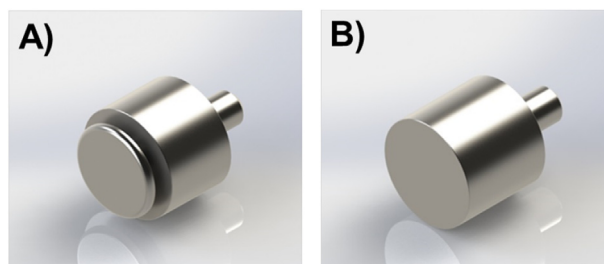
$$\varepsilon = -2\ln\frac{D(t)}{D_0} \tag{2}$$

$$\sigma_{zz} - \sigma_{rr} = \frac{F(t) - \frac{1}{2}m_f g}{\frac{\pi}{4}D(t)^2} \tag{3}$$

Here $D(t)$ and D_0 are the measured and initial diameter, respectively. $F(t)$ is the force on the bottom plate, m_f is the mass of the filament and g is the gravitational acceleration. Eq. (3) does not account for the initial shearing contribution due to the no-slip boundary condition on the plates [14]. The reason for omitting this contribution is that we did not use standard flat plates for this study as discussed in the following section.

2.2.1. Plate design for measuring non-sticky samples

The FSR-technique relies on the sample sticking to the end plates during the stretch experiment. Slip-off is an issue even for the most studied polymer in the FSR, polystyrene (PS). With PS, it is possible to circumvent this problem by increasing the prestretch i.e. increasing the area that sticks to the plate relative to the area of the midfilament plane. Increasing the prestretch was not sufficient in the case of the PE/PO solutions as the presence of PO resulted in greasy samples that slipped off very easily. To overcome slip-off, several new plate geometries were designed. The best design is shown in Fig. 1a and is in the following referred to as the "mushroom plate". The mushroom plate differs from the standard plate (Fig. 1b) in the way that it has an extra plate on top of the standard plate separated by a small rod. The additional plate and rod is referred to as the "mushroom".

The mushroom plate required a special moulding procedure inside the FSR in order to anchor the "mushroom" into the fluid. The moulding procedure is illustrated in Fig. 2. First the sample disc was sandwiched between the two plates and thick tin foil was wrapped around the plates. Second, the sample was heated to

Table 1
Material characteristics of the prepared solutions of UHMwPE in paraffin oil.

Sample	ϕ [w%]	T_m [°C][a]	T_m [°C][b]	Z
PE/PO-29%	28.7	123.5	119.2	960
PE/PO-17%	16.8	121.6	115.8	560
PE/PO-9%	8.8	118.9	113.6	293

[a] From DSC.
[b] From Eq. (1).

Fig. 1. Sketch of plate designs. (a) The mushroom plate design developed for stretching of non-sticky samples. (b) The original plate design for sticky samples.