Characterization of the primary and secondary crystallization kinetics of a linear low-density polyethylene in quiescent- and flow-conditions

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A B S T R A C T

The primary and secondary crystallization kinetics of a homogeneous linear low-density polyethylene were characterized as function of cooling rate, pressure and flow strength. Our approach to describe primary crystallization is based on nucleation and growth of spherulites, quantified well below the melting temperature using small-angle light scattering. The description of the two-step secondary process is coupled to primary crystallization using a convolution integral, for which the parameters were determined from (fast-) differential scanning calorimetry. Extended-dilatometry was used to investigate the effect of different thermomechanical histories. Parameters were determined for an existing model that couples molecular stretch to both nucleation rate and fibrillar growth rate. Excellent agreement is shown between calculated and experimentally obtained crystallization kinetics in conditions representative for those found in real-life processing conditions. This opens the possibility to calculate in detail the evolution of and the final crystallinity structure in products such as blown film or extruded tape.

1. Introduction

The use of ethylene and α-olefin copolymers has become widespread via the industrial implementation of metallocene type catalysts and the materials broad application in packaging industry. Also known as linear low-density polyethylene (LLDPE), the material is a substantially linear polymer with a large number of short branches, providing distinct rheological and mechanical properties, such as a relatively low shear sensitivity and a high tensile- and impact strength [1]. In order to understand the crystalline morphology of the final product as function of the shaping process, many researchers report on the crystallizability and processing-structure relation for various LLDPE resins, and focus specifically on the significant influence of the molecular branching-type, content, and distribution [2–7]. As the shaping process of polymeric products involves steep thermal gradients, high flow rates and pressure variations, studying the processing-structure relation in industrially relevant conditions requires well defined experiments in which these variables can be controlled. As a result of the rapid crystallization process of the ethylene based polymer, the temperature window for isothermal studies is often limited to low levels of undercooling. An additional complexity with branched (semi-crystalline) polymers is found in the high levels of secondary crystallization, sometimes up to 50% of the final crystallinity, due to a continuous insertion or thickening of lamellar features inside the spherulitic geometries [8]. Many different experimental techniques were used to study crystallization from the LLDPE melt, often providing a measurement signal in which the different processes cannot be separated (easily). Therefore, most researchers prefer combined techniques of, for example, small angle light scattering (SALS), differential scanning calorimetry (DSC), and/or simultaneous small- and wide-angle X-ray scattering/diffraction (SAXS/WAXD) to obtain detailed time resolved structural information [6,9–12]. Reports on the effects of flow on crystallization of LLDPE are limited and mostly performed using shear cell devices [7,13] or uniaxial extension [14], whereas the combined effect of pressure and flow has been studied mainly to obtain melt properties using rheometry [15,16].

In some studies, the experimentally obtained non-isothermal (quiescent) crystallization kinetics are used as validation or input

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for predictive structure calculations, often using kinetic models [17—19] or physical models describing primary crystallization [20—22]. In the case of LLDPE however, the most promising approach is found in extended Avrami models to account for secondary crystallization effects [23—25]. The latter suits the implementation of nucleation and growth functions to describe primary crystallization. Hence, such a model requires accurate determination of both, the spherulitic growth rate and nucleation density in a wide range of temperatures in order to correctly describe space filling of spherulites in time. In this work, we adopted an Avrami-type model for space filling based on nucleation and growth, combined with a convolution integral to accurately describe the evolution of primary and a two step secondary crystallization during quiescent non-isothermal solidification in a large range of cooling rates. To obtain parameter values, we use a combination of SALS, DSC and fast scanning chip colorimetry (FSC) techniques. Secondly, flow induced (primary) crystallization is described for different thermomechanical histories at multiple pressures with an approach based on rheology and dilatometry, similar to earlier work performed in our group [26]. Finally, dilatometry was used to characterize the effect of flow and pressure on secondary crystallization by converting the dilation measurement in a signal similar to those measured with DSC.

2. Material and methods

2.1. Material

The material investigated is a metallocene LLDPE (ExxonMobil). It has an average butyl branch content of 1.2 mol%, a weight average molecular weight, M_w, of 94 kg/mol and a number average molecular weight, M_n, of 24 kg/mol. The interchain branching distribution is relatively narrow, as indicated by temperature rising elution fractionation (TREF) data presented in Fig. 1 and molar mass fractionation of the same material reported elsewhere [27]. Details about the TREF procedure are included in Appendix A.

2.2. Methods

2.2.1. Thermal analyses

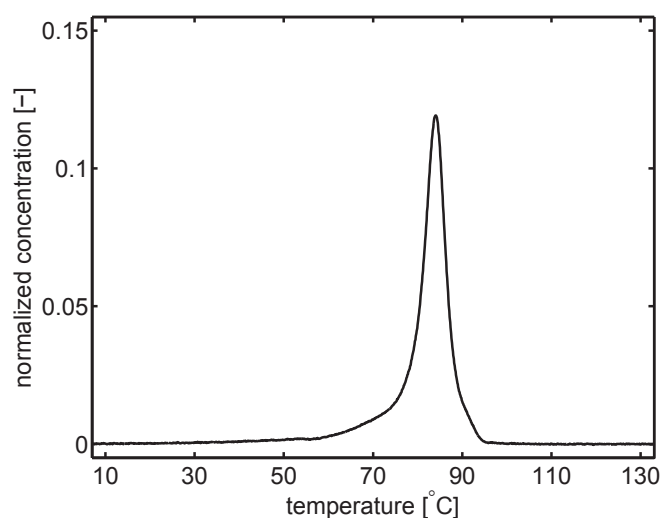Differential scanning calorimetry (DSC) was employed to investigate non-isothermal crystallization at relatively low cooling rates. Use was made of a Mettler-Toledo 823e/700 module in combination with a Cryostat intracooler. A sample of about 5 mg was placed in a 40 μm standard aluminum crucible. The sample was heated at 20 °C/min from 25 °C to 180 °C, held at that temperature for 5 min to erase any thermal history and subsequently cooled at rates, $\dot{T}$, of 4—20 °C/min to 0 °C. The equipment was calibrated for static temperature, thermal lag, and heat of fusion using indium and zinc. Nitrogen was used as a purging gas.

For relatively high cooling rates, non-isothermal crystallization was studied using a fast scanning chip calorimeter (FSC) Flash DSC 1 of Mettler-Toledo in combination with a Huber intracooler TC100 and UFS-1 sensors [28—30]. Samples were prepared by microtoming and microscope-aided cutting. The specimen was heated at 100 °C/s to 150 °C and kept at that temperature for 1 s, which is sufficient to remove all thermal history due to the limited sample dimensions. Subsequently, the sample was cooled to −50 °C in a range of 50—2000 °C/s. Scan rates below 50 °C/s were not investigated, the signal to noise ratio became unsatisfactory due to the low sample mass. Above 2000 °C/s, the cooling rate selected could not be maintained until the end of the crystallization process. Nitrogen was used as a purging gas, no corrections for thermal lag effects were included since the sample dimensions were considered minimal. The FSC sensor was conditioned and temperature-corrected according to the specification of the instrument provider.

2.2.2. Small angle light scattering

Small angle light scattering (SALS) combined with a temperature jump-stage experiments were performed to measure the temperature dependent spherulitic growth rate and nucleation density up to high levels of undercooling. Samples of approximately 5.5 mm in diameter, 30 μm in thickness and a mass of 0.5 mg were prepared by melt-compression molding a small amount of granular material sandwiched between two cover glasses of 9 mm in diameter and a thickness of 150 μm each. The specimens were placed in a custom-modified JHT-350 temperature-jump stage [31] (Linkam, Japan), which consists of two separately controlled heating stages and allows for the sample to be rapidly transferred from the hot stage, set to 150 °C, towards the cold stage, set at the desired temperature for crystallization, by means of an aluminum slide. The sample was transferred to and kept at the hot stage for 1 min to erase all structural history. Due to the large capacity of the heating stages and the small sample size, cooling rates were reported in the order of 300 °C/s [31]. Custom modifications by our group consist of a remotely controlled and air pressure driven actuator, connected to the aluminum slide, to quickly transport the sample back and forth between the stages and at reproducible speeds, see Fig. 2. Experiments were performed in duplo at each set temperature. The temperature of both stages was corrected using a calibrated K-type
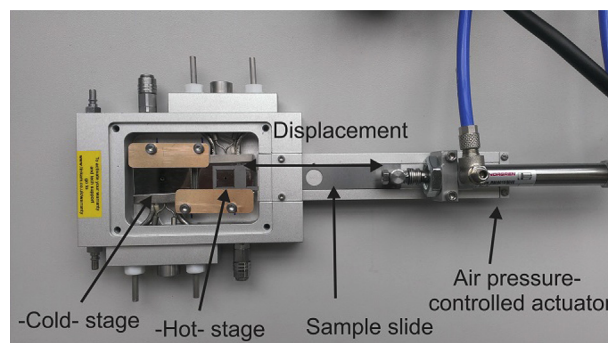

Fig. 1. Normalized concentration vs. temperature during TREF of the LLDPE investigated. The elution temperature directly relates to co-monomer content.

Fig. 2. The custom modified JHT-350 temperature-jump stage (without top cover).