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Structure evolution during film blowing: An experimental study using in-situ small angle X-ray scattering

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ABSTRACT

The on-line morphological development during film blowing of 2 different linear low density polyethylenes (LLDPEs) and a blend of LLDPE with low density polyethylene (LDPE) has been investigated, for the first time, using synchrotron Small Angle X-ray Scattering (SAXS). The processing conditions, blow-up ratio and take-up ratio, have been varied and the resulting lamellar thickness, linear crystallinity and orientation evolution in machine direction is obtained from a detailed analysis of SAXS data. Ex-situ SAXS and wide angle X-ray Diffraction (WAXD) confirmed the effect of molecular structure and composition on structure evolution observed in the on-line experiments. The results obtained provide a valuable set of data for the understanding of the film blowing process and can be used to extend and improve numerical model.

1. Introduction

Most plastic films and bags, ranging in sizes from sandwich bags to large films for agricultural uses, are made by the ingenious and engineering elegant process of film blowing. During this process a tubular film is extruded upwards through an annular die, blown up into a larger tubular film and cooled down by an external stream of cold air. The inflated, solidified tubular bubble is then flattened as it passes through the take-up rolls which also provide the axial tension needed to pull the film upward, and form an air seal so that a constant pressure, just above atmospheric, is maintained inside the bubble.

The process, although apparently simple, is rather complicated and challenging to understand: the solidifying polymer melt undergoes a combination of biaxial stresses and steep thermal gradients, leading to complex orientation, morphologies, and thereof properties, which are strongly dependent on the processing conditions used.

Another key issue concerns the tuning of final properties of the film by selecting the right material composition. For instance, polyethylene-based films are of great industrial relevance because of their relatively low production cost and easy processability: low density polyethylenes (LDPEs) were mostly used till a few decades ago because of their clarity, flexibility, sealing and barrier properties. Recent developments in metallocene-based synthesis techniques have brought into the market linear low density polyethylenes (LLDPEs) which show better mechanical properties and higher toughness. However LLDPEs show lower processability compared to LDPEs, such as high melt pressure and bubble stability, issues which are

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translated in surface irregularities causing high haze and loss of clarity [1,2]. To overcome these drawbacks, LLDPEs are usually blended with a small amount (up to 10%$_{wt}$) of LDPE resulting in an improvement in processability at the expense of the final physical properties.

Extensive research has been carried out on the materials or on the final morphology of the blown films using a wide range of experimental techniques, such as X-ray scattering [3,4], rheology [5,6], electron microscopy techniques [7,8], differential scanning calorimetry (DSC) [8] and FTIR trichroism [7]. Mostly off-line methods (also in industry) are used to modify the processing variables and material composition by trial and error until the optimal conditions are found. However, such a procedure is expensive and time consuming. A more systematic approach would be that of using data from real-time experiments to improve and validate already existing numerical models on the process [9–13]. In this way by applying these validated models the processing conditions could be modified a priori to get the desired properties. Despite the number of existing models, the amount of experimental data is far from being sufficient since only a few on-line studies were performed so far [14–18]. Moreover, the techniques used (wide angle X-ray diffraction, Raman spectroscopy, SALS and birefringence) were not able to study the structure evolution on a nano-scale while this is of fundamental importance, since mechanical and optical properties, including haze and clarity, are strongly dependent on morphological features such as lamellar thickness and crystalline superstructures, i.e. row nucleated structures, not detectable with the techniques just mentioned.

To fill in this gap, the present paper focuses on the morphological development and evolution on a nano-metric length scale, in the range 1–100 nm using, for the first time, in-situ Small Angle X-ray Scattering (SAXS). A well defined combination of machine settings as well as different materials are investigated in real time by mean of high energy synchrotron radiation, the structure evolution along the bubble from the die exit to well above the solidification line is provided and analyzed in detail. However, to confirm the on-line observation the final structure of the films is also analyzed by mean of ex-situ SAXS and WAXD measurements, the results were found in good agreement.

Compared to previous on-line studies, we think we provide a set of well defined and reproducible experiments, as confirmed by the strain and strain rates analysis of experiments performed on different materials at the same combination of processing conditions. Our results are closer to real processing if compared to the several studies of Gururajan [14,16] (blow-up ratios used of 0.6 and relatively low take-up ratios) and complementary to the studies of van Drongelen [15] and Bullwinkel [17] which employed WAXD and SALS, to investigate two completely different length scales.

The main goal of this work is to demonstrate the feasibility of an on-line synchrotron SAXS study on film blowing and to provide experimental data that can be used to validate numerical models for this process.

2. Experimental

2.1. Materials

The materials used for this study are two commercial linear low density polyethylenes (named LLDPE 1 and LLDPE 2 in this work) and a blend of LLDPE 2 with 10%$_{wt}$ of low density polyethylene (LDPE), all provided by ExxonMobil.

The two LLDPE grades, both prepared by metallocene catalysis, show similar molecular weight, different polydispersity indexes (PDI) and different amount of butyl-branching (2.1 and 6%$_{wt}$ respectively) Another substantial difference between the two is the comonomer interchain distribution: LLDPE 1 has a relatively narrow unimodal interchain comonomer content distribution while LLDPE 2 has bimodal and broad interchain comonomer content distribution [19,20].

Finally, the LDPE used for the blend has relatively higher molecular weight and polydispersity.

The most important molecular features of the materials are listed in Table 1.

2.2. Film blowing setup

A Collin Blown Film Unit type 180-400 and extruder were installed at the Dutch Belgian Beamline BM26B at the European Synchrotron Radiation Facility (ESRF, Grenoble, FR). A picture of the setup is shown in Fig. 1. The used die diameter and gap were 50 and 0.8 mm, respectively. Notice that the film blowing line is relatively small compared most blown film present in industry. However, in this work we tried to use processing conditions as close as possible to the one used in "real-life" processing.

During film-blowing, two main quantities govern the stretch in the machine direction and the amount of expansion of the bubble (related to the stretch in transverse direction), the take-up ratio (TUR) and the blow-up ratio (BUR), respectively. The

Table 1
Molecular characteristics for the materials used.

Material	M_w [g mol^{-1}]	PDI	Butyl-branching [%$_{wt}$]
LLDPE 1	94,000	3.9	2.1
LLDPE 2	108,000	2.4	6
LDPE	217,000	5.9	–