1 INTRODUCTION

Bimodal polyethylene is a kind of polyolefin with bimodal molecular weight distribution. Such bimodality may be simply achieved by producing the two components separately and then blending them together or producing each component in a two-stage series reactor [1]. With the introduction of bimodal polyethylene (PE) resins into the marketplace, the industry has been confronted with the need to understand the rheology and the processing of a new and different class of PE resins. However, due to their high molecular weight, difficulties in processing are often encountered. In the present work, the melt fracture especially surface melt fractures of the PE resins in capillary extrusion are studied.

The melt fracture behaviors of the conventional PE resins in capillary extrusion flow are well understood, and the physical mechanisms have been discussed in many reports [2–4]. In the capillary extrusion of the conventional PE resins, such as high density PE (HDPE) and linear low density PE (LLDPE), generally the flow instability can be classified into two types, one is rough surface, which is called as sharkskin failure, and the other is volumetric gross melt fracture. Surface melt fracture (sharkskin) occurs first at a low shear rate range. It is characterized by fine scale surface irregularity, which grows with increasing the flow rate. The gross melt fracture is shown as severe distortions due to the entrance pressure fluctuation at higher flow rate [5].

Only a few publications have studied the flow behaviors of the bimodal PE resins and polydisperse polymers [6–9]. It has been reported that the viscosities of the blends containing low molecular weight (MW) fractions decreased rapidly at high shear rates [6]. It is also found that the addition of low MW PE to a linear high MW PE significantly decreased the viscosities and caused a noticeable reduction in the magnitude of pressure oscillation and the degree of the flow curve discontinuity [7]. Schreiber performed capillary extrusion studies on a series of blends made of fractionated components of linear PE. He observed that the blends with low MW fractions distinctly reduced the magnitude of the flow curve discontinuity. He also found that the blends utilizing components with widely different MWs were far more effective in reducing the flow curve discontinuity than the blends with broader but more normally shaped distribution functions [8].

For the bimodal PE, the addition of low MW component drastically increased the melt flow index. It is found that the bimodal PE in the capillary flow showed more shear thinning behavior than the unimodal PEs of similar MW, suggesting that lower viscosities in extrusion flow could be obtained with the bimodal resins [10]. Most recently, Ansari et al [11] observed that the Cox—Merz rule was not valid for the PE resins with a broad MWD by comparing the viscosities measured from capillary test with the linear viscoelastic (LVE) data. Wall slip was suggested as the reason for the lower steady-state viscosities of the capillary test than the LVE viscosities. This paper studied
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the melt fracture behavior of a series of the bimodal PE resins as observed in capillary extrusion flow. The physical mechanisms of the melt fracture especially surface melt fractures are discussed.

EXPERIMENTAL

Materials

In this experiment, two series of unimodal and bimodal PE with different molecular weight distribution was chosen for this study. The naming convention of the samples identifies the kinds of polyethylene and the proportion of low molecular weight fraction (LMW)/ high molecular weight fraction (HMW). For instance, BE-2.06 denotes the sample is bimodal polyethylene and the proportion of LMW fraction/ HMW fraction is 2.06. UE-1 means the only unimodal polyethylene that we chose. The SEC curves of the three PE resins are shown in Fig. 1. There is a distinct separation of the two modes in the bimodal resins. The bimodal molecular weight distribution curves were fitted with two Gaussian distributions to estimate weight fractions, number average molecular weight \(M_n\), and weight average molecular weight \(M_w\) of the two components as listed in Tables 1 and 2. The relative compositions of the two components of the bimodal resins were systematically different. BE-1.47 has the most amount of LMW component and BE-3.17 has the highest \(M_w\) of HMW component. BE-1.47 and BE-2.81 has the lowest \(M_w\) of LMW component.

Gel Permeation Chromatography

The polymer samples were characterized for their molecular weight and molecular weight distribution using an Agilent 1100 LC high temperature gel permeation chromatograph (GPC). The mobile phase used was 1,2,4-trichlorobenzene and the temperature was 160°C (the sample were first dissolved in 1,2,4-trichlorobenzene for 10 h in the presence of 0.5 wt % of antioxidant to avoid degradation). The average molecular weights were determined by a universal calibration curve obtained using narrow MWD polystyrene standards.

Rheological Measurements

Dynamic rheological measurements were carried out in a Gemini 200 (Bohlin Instruments, United Kingdom) stress-controlled rheometer in constant-strain mode. The diameter of the plate was 25 mm, and the gap was about 1 mm. All of the samples were tested in the frequency range from 0.01 to 100 Hz at 200°C. To keep the response in the linear viscoelastic region, the applied strain was controlled at 1%. The thermal stability of the samples during rheological testing was checked by a time sweep and all of the tests were completed within 10 minutes.

High pressure capillary measurements were performed on a capillary rheometer (GOTTFERT Rheolograph 2002, Germany) at 200°C. A round hole die of 1mm diameter with a length/diameter (L/D) ratio of 16 was used. The range of apparent shear rates was between 20–2000 s\(^{-1}\). The rheological data were calculated directly on the rheometer.

RESULTS AND DISCUSSION

Figure 2 shows the flow curves of the four polyethylenes. PE develops sharkskin instability as a surface distortion was observed in the extrudate at low shear rates. As it has been proposed, the on-set of this instability can be related with a change in the slope of the flow curve [12–14]. Based on this change, it is found that the four polyethylene show different shear rate for the on-set of the shark skin instability as displayed in Fig. 1.

The photographs of the extruded stands are shown in Figs. 3–6. It is found from the figures that the four resins exhibit almost the same shear rate for the onset...