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A novel apparatus combining polymer extrusion processing and x-ray scattering

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ABSTRACT

A novel apparatus was designed and constructed combining polymer extrusion processing and x-ray scattering. It allows direct, real time monitoring of structure and temperature development in polymer material during extrusion. The apparatus involves a vertical industrial extruder equipped with a four-roll stretching device to mimic the processing environments of uni-axially oriented films or sheets, a simultaneous small and wide angle x-ray scattering system and an infrared thermometer as detection unit. The charging barrel of the extruder and the stretching device can be moved upward and downward precisely. By moving the sample along the center line, structure and temperature development as a function of position can be obtained. The performance of the apparatus was verified by a test experiment, which allows us to establish the relationship between processing parameters and evolution of structure with different length scales, and may lead to a better understanding of the physics in polymer processing.

1. Introduction

The end-use performance of polymeric products is strongly dependent on the microstructure [1] that develops during processing. In processes such as extrusion, fiber spinning, film blowing, etc., polymers are often processed from the molten state and subjected to intense and complex flow fields [2–4]. Processing flow can enhance the crystallization rate by orders of magnitude [5,6], induce anisotropic structures [7,8] and lead to new crystal forms such as β crystal of isotactic polypropylene (iPP) [9,10]. A better understanding of the structure evolution (precursor, lamellae and crystal) under processing conditions is crucial for optimizing industrial polymer production. Nevertheless, due to technological difficulties, only a few of works have been focused on the *in-situ* study of structure development during polymer processing [11–16].

Significant investigations have been made by different groups to mimic processing conditions and characterize the effect of flow. Sliding plate and rotating disk cells are commonly employed to impose simple shear [17–19]. Extensional flow is also realized by several types of extensional rheometers [20,21]. An injection molding type of flow cell was designed by Janeschitz-Kriegl [22], and then developed by Kornfield and co-workers [23]. However, in most cases, these devices could not reach the high level of strain and strain rate as typical processing conditions. Additionally, well-defined thermal history was usually applied in those experiments for simplified analysis. This implies that the results obtained may not be applicable to polymer processing directly, which often involves very intense and complex flow fields, high thermal gradients and cooling rates.

Different structure characterization techniques such as optical microscopy [24], atomic force microscopy [25], light scattering [26], birefringence [27,28], and x-ray scattering [29,30] have been applied to track the process of

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flow-induced crystallization, among which x-ray scattering is an excellent choice. X-ray scattering, especially combining small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS), is a powerful tool for investigating polymer materials because structural information of different length scales can be obtained simultaneously. Polymer processing is a complex time and spatial dependent process. Intrinsically, transient changing presents numerous challenges for investigation via x-ray scattering. Over the past few decades, many customized instruments have been developed to facilitate real time x-ray scattering measurements [20,21], but only a few works focus on the fundamental basis of effects of processing on structure [31–33]. Great progress has been made in the real time study of the structure evolution of fiber spinning using synchrotron radiation WAXS and SAXS, some of which revealed structural development of the order of milliseconds [11,14,34–40]. However, it is typically not easily accessible to carry out systematic work with synchrotron radiation due to limited beam time and space. In order to overcome the inconvenience of synchrotron radiation, a conventional laboratory x-ray source has been applied to real time study recently [14,15,31–33]. Structure development along the bubble during film blowing of low-density polyethylene was reported [15], but only WAXS was used to track the crystallization process. Simultaneous SAXS and WAXS were employed to study structure development in the spin-line of melt spinning [14]. However, structural feature larger than 20 nm could not be detected in this system due to the small distance between sample to detector and large size of beam stop, which is not enough for many polymers. A brief summary of the common features of above apparatus are listed below: (1) a piston-drive mono hole or laboratory-scale screw extruder was used for extrusion, in which the mechanical and thermal conditions are actually different with real processing; (2) a metering pump was employed to control the flow rate of melt in the charge barrel, which is not sufficient for precise experiment; (3) the precision of relative movement between sample and x-ray beam is in the order of millimeters, which corresponds to a low detection time resolution during crystallization; (4) a rotating anode x-ray source was utilized for x-ray measurements. The high flux and large divergence characteristics of this source make it suitable for WAXS but not for SAXS measurements. Even although simultaneous SAXS and WAXS can be conducted, long exposure time is needed to collect a scattering pattern.

Despite the success that has been achieved in applying x-ray scattering for *in-situ* measurements of structure development during processing, these methods should be extended to the widely used extrusion. Studying structure development during extrusion is a formidable challenge. The configuration of typical industrial extruders is horizontal, which is poorly suited for real time x-ray scattering because the incident x-ray beam is also commonly horizontal. Another large obstacle for *in-situ* study with a horizontal configuration extruder is the pendulous nature of the melt after exiting the extrusion die because of gravity. The gravitational effect has negligible influence on spinning due to the small dimension of fiber. In this work, a vertical industrial-scale extruder was customized to adapt for the beam path of x-ray, which also reduces the effect of gravity deformation of the melt. Servo motors were installed for accurate control of the flow rate of melts and movement of the extruder. A unique four-roll stretching device was introduced to mimic the complex processing environments of uni-axially oriented film or sheet A new low divergence x-ray source was chosen for x-ray measurements. Simultaneous SAXS and WAXS information during the crystallization process can be obtained, and additional capability for *in-situ* measurement of sample temperature also can be achieved.

2. Experimental apparatus

2.1. Overview

Fig. 1 is a schematic diagram of the apparatus. A mechanically modified vertical industrial extruder equipped with a four-roll stretching device is used to impart the desired thermal and mechanical history to the polymer. High flux x-ray is available from a homemade x-ray scattering system, which provides the necessary flux to acquire data of a transient process. Polymer pellets are fed to the charging barrel to be melted and then transported to the extrusion die. The stretching device is designed to perform *in-situ* x-rays scattering measurements easily. A 1D position sensitive detector (PSD) and 2D multi-wire detector are used to acquire WAXS and SAXS signals, respectively. *In-situ* sample temperature measurement can be made by an infrared thermometer. To allow measurements to be taken as a function of position, a leading screw was installed to accurately control the charging barrel and the stretching device upward and downward. Each component will be illustrated in sequence as follows.

2.2. Mechanically modified industrial extruder equipped with stretching device

The main designs incorporated in this extruder are listed as follows: (1) Two YASKAWA servo motors were installed as the driving unit to control the extrusion speed and lifting of charging barrel precisely. (2) A four-roll stretching device was designed and constructed combined with the extruder to simulate typical processing

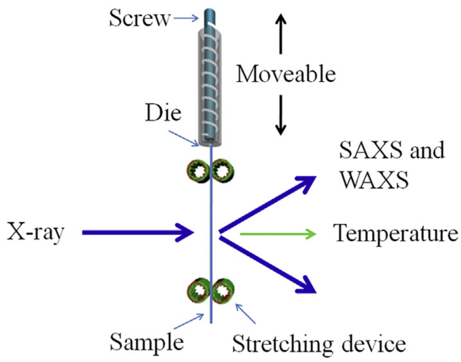

Fig. 1. Schematic diagram of the combined polymer extrusion processing and x-ray scattering apparatus.