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Material behaviour

In situ near-infrared spectroscopic studies of the structural changes in polyethylene during tensile deformation



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ABSTRACT

Structural and conformational changes occurring during tensile stretching of high-density, linear low-density, and low-density polyethylene materials were investigated with in-situ near-infrared (NIR) spectroscopy. Fragmentation releases the chain ends within crystalline lamellae and the cilia chains that are embedded in crystalline lamellae, and enables changes from the trans to gauche conformation. Meanwhile, the inclusion of co-monomers in the crystal lattice of linear low-density polyethylene causes the lamellar cluster to soften and stretch. Plastic deformation such as chain unfolding and slippage occurs within lamellar clusters.

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1. Introduction

The structural rearrangement of semi-crystalline polymers such as polyethylene (PE) and polypropylene (PP) during uniaxial tensile stretching has been of significant academic and industrial interest. A number of studies concerning necking and yield behavior under uniaxial tensile deformation have shown that crystalline morphology strongly affects properties that result in structural failure and plastic deformation; however, the molecular mechanisms in tensile failure are not completely understood and remain controversial. This is due to the paucity of in-situ data concerning structural morphology and chain conformation during stretching.

The necking phenomenon was first discovered by Carothers and Hill in 1932 [1], when they observed it in filaments of semi-crystalline polyester. Flory and Yoon [2] demonstrated that yield and necking processes in semi-crystalline polymers are caused by a local-melt re-crystallization process, and that local adiabatic heating at the neck area induces melting of the crystal lattice. Peterlin et al. [3–5]

have concluded that the necking and yielding of PE leads to large-scale transformation from lamellar crystals to a fibril structure. The expanded model of melt re-crystallization was proposed by Gent et al. [6,7]. The stretching temperature is the most important factor in the partial melting of folding chains. However, Brauer et al. [8], Vincent [9], and Lazukin [10] all found that necking takes place even at a very low stretching rate. In addition, Allison and Ward [11] demonstrated that the adiabatic increase in temperature is too small to explain a local-melting process. Leonov [12] examined a theoretical kinetic model for necking based on the unfolding of crystalline chains discussed by Gent et al.

Nitta and Takayanagi [13,14] proposed a lamellar cluster model for explaining the yielding mechanisms of semi-crystalline polymers such as PE and PP. According to this model, lamellar clusters (several stacked lamellae) act as a deformation unit at the yielding and necking region, and the stacked lamellar clusters fragmented into cubic cluster units, the size of which corresponds to the end-to-end distance of the chains. Concerning post-yielding processes, Kuriyagawa and Nitta proposed a theory as an extension of the lamellar cluster model [15]. By measurement of the natural draw ratio of high-density PE (HDPE) samples under a slow stretching rate, they discovered that

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Poisson's ratio remains 0.5 throughout necking and is independent of crosshead speed. In other words, a neck is understood to be a perfect plastic deformation under a slow tensile stretching rate. They examined that lamellar cluster units rotate and closely pack during yield deformation into a stacked lamella cluster at the shoulder region of the neck like a "wall." During neck propagation, the frontier layer (or "frontier wall") catastrophically collapses due to the sliding cluster units, where a cluster unit is treated as a rigid cubic body and is not deformed. The cluster units that are embedded in the sectional frontier wall in the necked region are rearranged into cuboidal objects during the necking process.

Rheo-optical techniques rely on optical parameters that are associated directly with structure and intermolecular interactions; thus they have been used to examine the molecular basis of deformation behavior under tensile deformation [16–20]. Infrared (IR) spectroscopy is the most common spectroscopic technique to detect molecular orientation and chain conformation states of crystalline polymers such as PE and PP. In-situ Fourier transform IR spectroscopic studies of conformational changes for PE and PP films have been conducted. The mid-infrared (MIR) region from 2500 - 25000 nm can be used to diagnose changes in these polyolefins. However, high absorption of MIR during transmission makes it difficult to identify spectra for thick specimens, thus requiring the preparation of thin films (<100 μm thickness). With near-infrared spectroscopy (NIR), however, one may analyze the deformation process or orientation behavior of thicker polymeric materials and plastic products. In a recent study, we demonstrated that the orientation of the main CH_2 chains in 500 μm thick PE sheets may be obtained by simultaneous NIR spectroscopy and tensile deformation measurements.

The NIR region primarily consists of contributions from combination and overtone bands generated by anharmonic molecular vibrations. Since these absorbances are much weaker than the basic fundamentals, much thicker samples can be used. However, a disadvantage with NIR spectroscopy is that overlapping overtone and combination bands make them difficult to assign. In a previous paper, the computational and experimental data for normal alkanes during melting [21] made it possible to assign several PE NIR bands.

In this work, we simultaneously measured NIR spectra and tensile stress in order to examine the deformation behavior of relatively thick PE sheets having different crystallization behavior in the yielding and necking region. The significance is to provide a novel method for the characterization of molecular and/or structural states in materials and industrial products that are under deformation.

2. Experimental methods

2.1. Materials and sample preparation

High-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) were supplied by TOSOH Corp. The molecular characteristics for each are given in Table 1.

Table 1
Molecular characteristics of the samples.

Sample	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
HDPE	10	1.7	5.9
LLDPE	11	2.6	4.2
LDPE	20	2.2	9.1

The PE pellets were melt-pressed in a laboratory hot press at 210 $^\circ\text{C}$ and 10 MPa for 10 min, followed by quenching at 0 $^\circ\text{C}$. The thickness of the compression-molded samples was 500 μm .

2.2. Characterization

The crystallinity of sheet samples was estimated by the Archimedes method using a METTLER electrobalance XS205 with ethanol as the solvent. Densities of the crystalline and amorphous regions used for the crystallinity calculation were 1003 and 852 kg/m^3 , respectively [22]. Structural characteristics of the samples are shown in Table 2.

2.3. NIR spectral measurements during uniaxial tensile deformation

The NIR experimental arrangement (Fig. 1) consisted of xenon short arc lamps (USHIO Inc. UXL-300D-O), an InGaAs PIN photodiode (Hamamatsu photonics Inc. G8371-03), and a monochromator (JASCO Co. CT-10). A digital oscilloscope (Lecroy Co. Model 9310L) was used for data acquisition and was computer-controlled, together with the monochromator, by an in-house program using Igor 4.0 (Wavemetrics Inc.). A GP-IB board (CONTEC Co., Ltd. GP-IB(PCI)F) was used for computer interfacing.

The tensile tester was specially designed for upper and lower clamps to symmetrically move from the central point of the film. The beam spot remains at the initial position throughout stretching.

The specimen was notched at 2 mm intervals along its length and 4 mm along its width, and the crosshead speed was fixed at 1 mm/min. The monochromator slit was 4 mm in length and 0.5 mm in width.

3. Results and discussion

NIR spectra from 1650 to 1900 nm for the PE samples under uniaxial stretching are shown in Fig. 2. It was found that the intensity of the spectra decreases with increasing strain; this was due to sample thinning during stretching. Therefore, variations of the NIR bands as a function of strain were normalized by the total peak intensities.

Table 2
Structural characteristics of the samples.

Sample	Crystallinity/%	Density/ $\text{kg} \cdot \text{m}^{-3}$
HDPE	59	940
LLDPE	41	915
LDPE	37	909

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