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Test Method

Analysis of Mullins effect in polyethylene using ultrasonic guided waves

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ABSTARCT

Small strain deformations below yielding can cause plastic deformation in semicrystalline polymers by a process similar to what is described for filled rubber-like materials known as the Mullins effect. Inter-lamellae chains contribute predominantly in deformations at this level, and the residual plastic strain can be attributed to permanent damage to the tie chains, affecting the long-term mechanical resistance of a molded part. With little detectable alteration of the polymer crystallinity at this early onset of plastic deformation, the primary characterization method applied to date is cyclic tensile loading, which provides information of stress-softening by monitoring the unloading path or relaxed stress behavior. An alternative method for monitoring the development of Mullins effect is proposed that can examine a molded part by using selected modes based on ultrasonic guided waves analysis. The technique was examined to determine if it could follow this effect induced by cyclic strain-controlled tensile deformations since it does not require sample preparation and could ultimately be applied while a part was in-service. Results for different polyethylene grades agree in trend with relaxed stress values over four cycles for tests of increasing applied tensile strain, demonstrated by an increase in the attenuation of ultrasonic guided waves. The correlation reveals a good promise in applying this method to structural health monitoring of plastic parts, while in use, to follow the initiation and progress of early service damage.

1. Introduction

Polyethylene (PE) will undergo non-linear elastoplastic deformation under tensile load before reaching its maximum stress. Although the yield point is a clear transition onto plastic deformation, the initiation of permanent damage can occur well before this transition [1]. Even small strains have been demonstrated to be capable of producing rearrange of the semi-crystalline structure, affecting long-term mechanical properties [2]. The stress-strain response of semi-crystalline polymers at small strains below yield corresponds to deformations of the inter-lamellae amorphous phase [3]. The separation of crystallites promotes the stretching and rupture of bridging chains that interconnect crystallites, resulting in permanent plastic damage [4]. Macroscopically, in cyclic mechanical testing, it is possible to observe this damage characteristic of the Mullins effect, mainly recognized by an observable strain-softening along the unloading path of the stress-strain curve and a non-recoverable residual strain after only the first cycle [5]. This effect is a result of the rupture of connection points (tie chains) in the crystalline network, being dependent on the history of maximum stretching and is a key characteristic to understanding the resistance of materials to crystalline slip that leads to yielding [6]. Based on this subtle damage, the Mullins effect is considered to reflect properties that are intrinsically correlated with long-term mechanical stability of parts molded with semicrystalline polymers. Since the primary method of assessing the Mullins effect is strain-controlled cycling mechanical testing, which requires detailed data recording, sample preparation and interpretation of stress-strain curves, the development of alternative techniques is currently sought by companies concerned with aging behaviors of their products, either for use in quality assessment or monitoring a part while in service.

Macroscopic, characteristic changes such as significant permanent variation of dimensions or sample discoloration can be visually observed but only after major plastic deformation beyond yield point of a semicrystalline polymer [7]. Considering microscopic structural observations, current experimental methods used in the

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detection of plastic deformation include small-angle X-Ray scattering (SAXS) [8], near-infrared spectroscopy (NIRS) [9], and Raman spectroscopy [10]. Such methods experience difficulties in detecting plastic flow initiation at early stages of deformation as they depend on the presence of cavitation or significant crystal deformation and orientation, that are only present closer to yield [11]. The non-crystalline phase of PE has a significantly greater role in dislocations during viscoelastic deformation due to its lower bulk modulus [12]. Therefore, in order to promote early detection of plastic deformation it is essential to develop practical methods capable of characterizing changes in the interconnectivity of crystallites and non-crystalline phase mobility. However, current methods that have demonstrated successful results such as atomic force microscopy (AFM) [4] and nuclear magnetic resonance spectroscopy (NMR) [13] require highly specialized sample preparation and testing procedures, restricting their practical application in industry.

Ultrasonic techniques are non-destructive characterization methods that analyze the manner by which sound waves are altered upon propagating through a medium to reveal microstructural details, such as information related with thermomechanical and morphological properties. Important contributions from Nitta and collaborators have demonstrated the effectiveness of ultrasonic methods using parameters of bulk wave velocity and signal attenuation to analyze the plastic deformation of semi-crystalline homopolymers and polymer blends under oscillatory and uniaxial tensile deformation [14–16]. Increase in ultrasonic velocity and attenuation was correlated with orientation of crystallites and the occurrence of cavitation due to large strain deformation. The dispersive nature of semi-crystalline polymers requires a spectroscopic analysis of the ultrasonic signal since attenuation for such materials is frequency dependent [17]. Recent improvements to materials characterization have been achieved with the use of ultrasonic guided waves, a method that presents advantages to characterization of highly attenuative materials. The interference phenomenon of reflective waves on plate walls allows propagation over longer distances, combined with the analysis of dispersive properties of semicrystalline polymers providing features of bulk macroscopic properties of the investigated sample [18,19]. Therefore, this paper will focus on demonstrating the use of ultrasonic guided waves to analyze plastic deformation at its early stages in different polyethylenes (high density, linear low density and bimodal). The novelty of the study is showing that parametric descriptors of the ultrasonic signal are correlated with the initiation of plastic deformation when using small strain-controlled tensile deformation testing to detect Mullins effect. Demonstrating the practicability of ultrasonic techniques to the observation of interlamellae alteration of semi-crystalline polymers undergoing plastic deformation is an important advance to the development of a suitable characterization methods under Industry 4.0, and can be later exploited as non-destructive evaluation for in-line process monitoring or in-field early failure detection.

2. Materials and methods

2.1. Materials

Four commercial grades of polyethylene were supplied by Imperial Oil Ltd (Sarnia, ON). Table 1 provides a summary of the grades, listing their corresponding density, melt index (MFI; measured according to ASTM D1238) and environmental stress cracking resistance (ESCR; measured according to ASTM D1693A) which were determined by the supplier for this work, and includes PE Grade numbers which will be used to reference these samples in this study. The grades varied from homopolymer high density (HD) to linear low density (LL) polyethylene, with different degrees of hexene used as copolymer. A bimodal grade (HD.B) is included in the study with intermediate values in terms of density and ESCR. All samples were prepared as plaques by compression molding the resin for 5 min at 190 °C and then quenched using water-cooled plates. Rectangular test specimens of approximately 20 mm (width) x 180 mm (length) x 3 mm (thickness) dimensions were cut from the 180 mm × 180 mm plaques.

Table 1
List of PE grade studied and selected properties.

Grade	Type	Density (kg/m^3)	MFI (g/10min)	ESCR (hours)
HD1	Homopolymer	965	8.8	2
HD.B	Bimodal	956	0.3	775
HD2	Copolymer (Hexene)	943	2.1	554
LL	Copolymer (Hexene)	933	5	>1008

2.2. Mechanical characterization

Strain-controlled tensile testing was performed using a 10 kN benchtop Model 3366 Universal Mechanical Testing System (UMTS, Instron Corporation; Norwood, MA). The rectangular samples were pulled longitudinally with a strain rate of 1.4×10^{-3} s^{-1}. Young's modulus was calculated from the stress-strain data to represent specimen stiffness. Two tests were performed: a varying strain test and a cyclic test. Every test was stopped at a specific strain, above the proportionality limit but before the yield point, at which time the specimen was held at that fixed displacement to observe its relaxation stress for an additional 20 min. For the varying strain test, samples were tested for elastoplastic deformation at strain values of 0.5, 1, 2, 4 and 8%. For the cyclic strain-controlled test, each sample was submitted to four consecutive cycles of a fixed value of 2% strain followed by relaxation with intervals of 20 min, and in between each cycle the sample was removed for ultrasonic measurements. In each cycle, three points of the cross-section of the sample were measured with a caliper for thickness and width dimensions. The tensile tests were performed at ambient room temperature. Reported experimental variability was based on a 95% confidence interval from three repeats for each grade.

2.3. Ultrasonic test

Pulse transmission testing to produce ultrasonic guided waves within the specimens was performed using a Panametrics NDT C604 (2.25 MHz-1.0″) ultrasonic transducer as an emitter and a Physical Acoustics F30α as a broadband receiver sensor. The emitter and sensor were positioned on opposite faces of the rectangular shaped samples at 85 mm distance from their center points, using Dow Corning high vacuum grease as a coupling agent. Excitation of the undeformed and strained samples after being taken from the UMTS was done with a square wave pulse of controlled frequency produced with an Agilent 33210A waveform generator. The received signal was amplified using a Physical Acoustic 2/4/6c amplifier set to +60 dB. Acquisition was done at a sampling rate of 4 MHz using a National Instruments Corporation 10 MHz 12-bit 4-channel data acquisition card and a LabVIEW™ (National Instruments Corporation) software environment to create separate files for each pulse registering an amplitude over a threshold of 0.06 mV.

Each test consisted of creating 25 pulses of different emitted frequencies (f) varying from 360 to 600 kHz at a step size of 10 kHz; for all polyethylenes with the specific geometry tested, signals above 600 kHz showed modes with low signal-to-noise ratio due to high attenuation, whereas for modes below 350 kHz, the identification of dispersion modes was affected by overlapping waves. The