

**Effects of Annealing and Swelling to Initial Plastic Deformation of Polyethylene probed by  
Nonlinear Ultrasonic Guided Waves**

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Submitted to: POLYMER

August 2017

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## **ABSTRACT**

Identification of precursor events related to incipient plastic deformation in polyethylene parts using a nondestructive technique is investigated in this study. A pair of ultrasonic transducers mounted on the surface of a test sample were used to propagate ultrasonic pulses of varying frequency while progressively small flexural deformations below yielding were applied. The evolution of higher order harmonics were observed in association with increasing micro-structural modification. Three different polyethylene grades were molded using different thermal treatments. Results showed that different crystalline networks could be correlated to different mechanisms of plastic deformation that was observed by a defined ultrasonic parameter under proposed method. Variation of the ultrasonic parameter was similarly observed with the residual stresses associated with solvent swelling, as studied by penetration of toluene in the bimodal and copolymer grades. Results and discussion presented in this study connect this non-destructive characterization method with mechanisms of incipient plastic deformation in polyethylene.

**Key-words: Nonlinear Ultrasonics, Plastic deformation, Polyethylene**

## 1. Introduction

Understanding the mechanisms of plastic deformation is essential for prediction of long-term sustained service of polyethylene (PE) parts. Initiation of yielding corresponds to a non-linear response to deformation prior to permanent structural damage, which is directly associated with the concentration of internal stresses causing crystalline dislocation [1]. Heterogeneous crystalline lattice formation is an essential physical element providing the strength resistance and unique plasticity of semi-crystalline polymers compared to amorphous polymers [2]. Although the degree of crystallinity is an important parameter influencing this early stage of plastic deformation for PE, another important factor controlling crystalline dislocation is the morphology of its inter-lamellae crystalline regions [3,4]. These regions are comprised of stress transmitters across the crystal lamellae boundaries known as tie chains, that are associated with the mobility of the macromolecular network and are known to control structural changes arising during these early stages of deformation [5–7]. Processing history, particularly the associated crystallization kinetics, for a semi-crystalline polymer directly impact the density of these tie chains, which in turn significantly influences the slow crack resistance of formed parts [8–10]. The inter-crystalline region can also be affected by penetration of low molecular weight contacting fluids, which can similarly promote internal stresses [11]. Therefore, connecting mechanical and environmental stresses through characteristics of the inter-crystalline network is important to predict the plasticity and long-term performance of PE parts.

Above the proportionality limits of elasticity, internal microstructural damage leads to an accumulation of residual stresses attributable to crystal shear, lamellae separation/cavitation and/or crystal stretching [12]. Currently, a limited number of characterization methods can be applied to observe structural changes at the onset of plastic deformation. Local strain deformation can be observed at the microscopic level through the long period of crystals using *in situ* small angle X-ray scattering (SAXS) [4,13]. Orientation by plastic deformation is demonstrated by *in situ* Raman

spectroscopy [14]. Mobility of different semi-crystalline domains can be measured using nuclear magnetic resonance spectroscopy (NMR) [15]. Permanent damage due to crystalline fragmentation has been visualized by atomic force microscopy (AFM) [16]. Additionally, the energy from cavitation and crystal damage can be recorded using acoustic sensors [17]. Although, these methods are effective in the investigation of some elements of initial plastic deformation, they provide micro to meso-scale analysis of local events, which has a limited applicability to predict macroscale events that occur in the long-term service of these parts [18]. From a practical perspective, none of the current experimental methods can characterize the bulk plasticity of PE samples.

Conversely, characterization methods based on ultrasonic guided waves are promising non-destructive alternatives that can be used for damage monitoring in bulk samples [19]. The non-destructive qualities and capacity to assess the bulk nature of materials by such methods lend themselves well to inclusion as sensing technology in advanced manufacturing platforms [20]. Recent evidences have shown the application of such methods to observe post-yielding lamellae to fibrillar transformation [21] and strain-softening after small cyclic deformation [22] for PE samples using tensile tests. The complexity of the propagated signal often requires further processing and spectroscopic analysis. A promising spectroscopic characterization is the use of detected variations in the amplitude of higher harmonics, also referred as nonlinear ultrasonic evaluation [23]. The use of nonlinear ultrasonic guided waves methods to follow the degree of plastic deformation has been demonstrated in metals [24–27], which are comparatively homogeneous in their structure, but also to detect localized damages in composites [28]. The suitability of the nonlinear ultrasonic approach has yet to be experimentally demonstrated with semicrystalline polymers, being only previously described theoretically for a second harmonic resonance [29] and for linear elastic regime [30,31]. Based on the elements demonstrated, this paper presents the use of nonlinear ultrasonic guided waves to evaluate incipient plastic behavior in modified polyethylene samples before yielding and assess the influence of

their crystallization history or chemical swelling in the performance of prepared parts.

## **2. Materials and Methods**

### *2.1. Materials*

Three different grades of polyethylene were supplied in pellet form by Imperial Oil Ltd. (Sarnia, ON). These grades included a reference homopolymer (HO) grade with density of 965 kg/m<sup>3</sup> and melt flow index (MFI) of 8.8 g/10min and two modified grades, namely: a hexene copolymer grade with bimodal distribution (BM), density of 956 kg/m<sup>3</sup> and MFI of 0.3 g/10 min; and, a hexene copolymer (CO) grade with density of 933 kg/m<sup>3</sup> and MFI of 5 g/10 min. Reported data on density and MFI were measured and provided by the supplier.

### *2.2. Specimen Preparation*

Samples of each polyethylene grade were compression molded into 180 mm x 180 mm x 3.2 mm thick plaques using a laboratory Carver press with heated platens. Pellets in a mold were initially heated to 145 °C for five minutes and then increased to 170 °C for additional five minutes, with gradually increasing pressure up to 10 MPa across the two stages of heating. With the polymer fully melted and compressed, two different thermal treatments were applied, namely: i) rapid quenching (Q), where the mold was water cooled at a rate of approximately 72 °C/min till reaching 80 °C, while maintaining pressure; or ii) annealing (A), where the platen temperature was reduced to 100 °C at the same previous cooling rate and then kept constant while the sample was held at pressure for one hour. After each treatment, the sample plaque was removed from the mold and allowed to further cool in ambient air. Flexural specimens with dimensions of 180mm (length) x 20mm (width) x 3.2mm (thickness) were cut from the plaques. Tensile samples with Type IV dimensions accordingly with ASTM D638-14 were prepared in a split mold using the same melting and thermal treatment procedures described above.

For studies involving chemical swelling, flexural and tensile specimens of each sample were

immersed in toluene (laboratory grade, Caledon Laboratories) for 15 and 48hrs at room temperature. After removal, samples were kept in the fume-hood for 30 minutes and wiped cleaned with paper towel to remove any excess of the chemical from the surface before testing. Weight of each sample was measured before immersion and after removal from the fume-hood using a Mettler Toledo analytical balance (model AE200).

### *2.3. Tensile and Flexural tests*

Mechanical characterization of the samples was done with a Model 3366 benchtop universal mechanical testing system (Instron Corporation) at room temperature and a relative humidity of 35%. Under tensile deformation, appropriate specimens were constantly strained to failure at a crosshead speed of 100 mm/min. Studies on flexural deformation were performed using a three-point method with a 65 mm support span. Specimens were progressively deformed to different degrees of strain (0.5, 1, 1.5 and 2%) in a step-wise manner at a crosshead speed of 2 mm/min. After being strained to one of these conditions, a specimen was allowed to relax with the return of the crosshead to its original position and ultrasonic testing was then performed while still in place before continuing to the next strain state.

### *2.4. Ultrasonic test*

With a specimen positioned for three-point flexural testing, two ultrasonic transducers were coupled to its surface using high vacuum grease (Dow Corning), each at a distance of 35 mm from the center where the crosshead tip would press to deflect. A 150 kHz resonant transducer (Physical Acoustics) was used as the signal emitter and a 350 kHz broadband sensor (Physical Acoustics) as the receiver. The signal was induced using a waveform generator (Agilent) to create a 10-cycles pulse, with each pulse at a predefined yet different frequency varying from 135 to 165 kHz by steps of 1 kHz. The received signal was recorded using a data acquisition system (National Instruments) with 4 MHz acquisition rate. Amplitude of time-domain events is reported in decibels (dB) converting the maximum

recorded level using a reference threshold of 0.06 V. Each event was converted to frequency domain using fast Fourier transformation, totaling 31 spectra being collected per strain condition. The collected data was analyzed using code programmed in Python language to calculate an 'ultrasonic parameter' that was based on the ratio of the third harmonic amplitude (A3) to the amplitude at the emitted frequency (A1). In order to allow the comparison between samples with different attenuation, results reported in this study follow the progress of the ultrasonic parameter using the amplitude ratio normalized based on the parameter value for the same sample before the first step in flexural strain was applied. The selection of the frequency range for the higher harmonics was based on previously identified guided wave modes that were suitable to characterization due to their low attenuation [22].

### *2.5. Differential Scanning Calorimetry (DSC)*

DSC tests were performed in a TA Instruments (model Q200) to analyze the melting peak of crystals from samples with different thermal histories. Samples of approximately 8 mg were tested in hermetically sealed Tzero pans. With a heat ramp rate of 10 °C/min, heat flow was recorded between 23 °C and 180 °C. The environmental chamber was kept with a constant nitrogen gas flow of approximately 50 ml/min. The content of crystals was calculated based on the enthalpy of the melting endotherm relative to an enthalpy of 290 J/g for purely crystalline PE [32].

### *2.6. Modified Bent Strip test*

For the long-term characterization of the PE samples, a modified bent strip test, adapted from the ASTM D1693 was performed. Strips with 115mm (length) x 20mm (width) x 3.2mm (thickness) were simultaneously bent into a U-shape with a 15.88mm radius and notched (0.5mm deep) with an in-house developed rig. The U-bent sample was mounted in a custom-made retaining device against an affixed 0.1 kN force sensor, allowing compression forces to be recorded over the test time. This test was capable to provide detailed information about the progression of slow crack growth. Analysis was made based on the crack growth time which is defined as the difference between the time of crack

initiation (defined as the point of inflexion of the force after full stress relaxation) and the time of fracture.

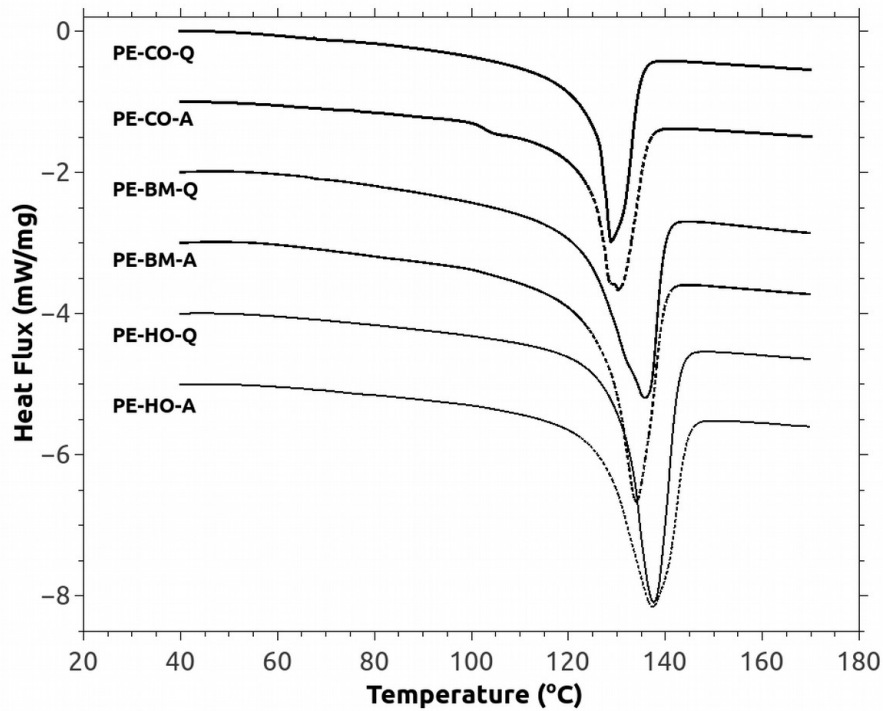
### 3. Results

Over the two following sections, characterization of PE properties is given for the different grades with different thermal processing histories (Section 3.1). These results based on traditional destructive tests serve as reference to correlate with the proposed nonlinear ultrasonic results in Section 3.2. Complementary observations of the ultrasonic method are presented in Section 3.3 with varied swelling states based on exposure of PE to toluene. Discussion is presented in Section 4.

#### 3.1. *Effects of Annealing on PE properties*

Figure 1 shows the DSC thermograms of samples prepared from different grades and thermal histories. The PE grades are indicated based on their unique structural characteristic: homopolymer (HO), bimodal distribution (BM), and copolymer (CO). A general increase in the endothermic peak, from 8 to 12 J/g can be observed in the annealed (A) samples compared to the quenched (Q), pointing to a higher degree of crystallinity in the former cases. The transition exhibited a single, though wider, peak in the thermograms of both annealed BM and HO samples compared to their respective quenched conditions, demonstrating the effect of prolonged crystallization time to promote growth of the lamellae thickness [33]. In contrast, the thermogram of annealed CO presented a noticeable secondary crystallization peak at 105 °C located closer to the annealing temperature, in addition to its peak transition temperature at 130 °C. This form of shoulder in the transition profile might be an indication of the organization of smaller crystals from mobile chains that were “frozen” in the amorphous phase in the quenching process. This effect can happen in parallel to the lamellae thickening of the main crystallization peak [34].





**Figure 1 – DSC curves of PE samples for different thermal treatments**

The effects of thermal history on crystallinity and mechanical properties for the different resin grades are presented in [Table 1](#). Elastic properties, namely flexural modulus and yield stress, can be directly correlated with changes in the total crystal content, with both increasing for the annealed sample versus quenched samples from all grades. Crystallinity increased between 2 and 7 % from quenched versus annealed samples, while flexural modulus increased between 4 and 10%, respectively. Properties knowingly related to the plastic behavior of semi-crystalline polymers showed some divergent results among the three resins. A reduction in elongation at break was observed for annealed HO and BM compared to quenching. Reduction in plasticity caused by annealing also affected crack propagation, as results in [Table 1](#) show a small reduction in crack growth time for HO and a significant decrease for BM. The lower resistance to crack propagation of an annealed specimen can be related to a lower concentration of tie chains, with the number of tie chains reported as being inversely proportional

to the lamellae thickness [7]. Conversely, annealed CO showed a general increase in plasticity based on strain at break values. Secondary crystallization seen by DSC in the CO samples might have created a reinforcement of the macromolecular network, responsible for increasing its yield stress and enhancing its plasticity [33]. Other short-term mechanical properties that could only be observed for CO samples under tensile load, and not for HO or BM, were natural draw ratio (NDR) and strain hardening (SH). The CO samples demonstrated a significant increase from quenched (NDR = 1.86, SH = 10.6 MPa) to annealed (NDR = 2, SH = 14.4 MPa) samples for both properties. Both properties are expected to correlate with concentration of tie chains [29]. Therefore, these results presented corroborate the earlier observation by DSC of secondary crystallization, in this case having a dominant effect on the plasticity of CO samples compared to any changes in tie chain density.

**Table 1 – DSC and mechanical characterization results for PE grades with different thermal history**

Material	Crystallinity – DSC (%)	Flexural Modulus (MPa)	Tensile - Yield Stress (MPa)	Tensile – Elongation at break (%)	Slow Crack Growth Time (h)*
PE-HO-Q	75.4 ± 1.0	1265 ± 100	29.8 ± 0.3	17 ± 2.0	3.9
PE-HO-A	77.0 ± 1.1	1343 ± 129	27.1 ± 1.0	4 ± 1.7	3.1
PE-BM-Q	75.7 ± 1.0	1086 ± 61	25.4 ± 0.9	60 ± 37	73
PE-BM-A	77.5 ± 1.1	1143 ± 86	28.2 ± 1.0	24 ± 6.1	38
PE-CO-Q	56.6 ± 0.8	749 ± 16	18.2 ± 0.2	197 ± 4.3	47
PE-CO-A	61.1 ± 0.9	674 ± 77	22.0 ± 0.5	255 ± 42	57

*\*Standard deviation for these results was not determined*

### 3.2. Nonlinear Ultrasonics

Traditional ultrasonic characterization relies on information drawn from the amplitude of an ultrasonic signal in the time domain. [Figure 2](#) demonstrates how maximum recorded amplitude from each polyethylene grade of differing thermal histories are correlated with flexural modulus. As the modulus decreases with declining crystal content, attenuation of the ultrasonic signal increases. This is a reliable non-destructive estimation of the density and stiffness of the crystalline structure prior to

incipient plastic deformation. However, no information can be drawn on the plastic behavior of these samples from such analysis. No significant differences between annealed and quenched samples are observed by this manner of characterization. Therefore, a new approach is proposed to characterize the initial plastic deformation using nonlinear ultrasonic guided waves.

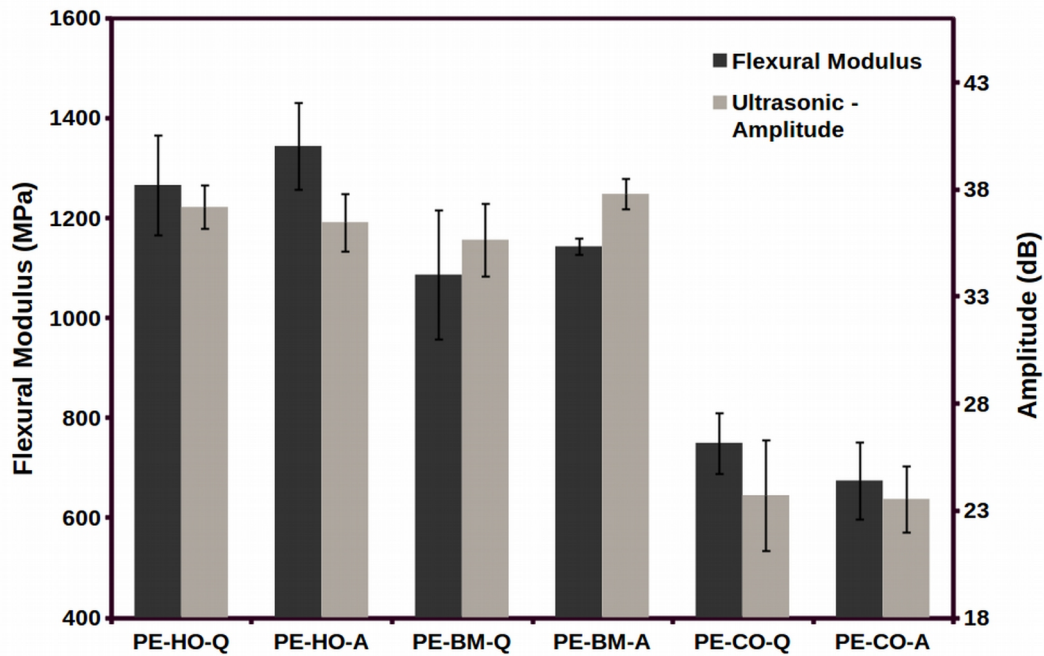


Figure 2 – Flexural modulus and ultrasonic signal amplitude of PE samples with different thermal treatments

Figure 3 shows how the amplitude of the third harmonic (A3) grew with increased flexural deformation in the elasto-plastic region well before yielding (expected at 5 to 6 %). Observations of these harmonics are only possible due to nonlinearities in the structure of the material, thus this differentiates the analysis from the traditional ultrasonic methods [23]. The amplitude ratio between the third harmonic (A3) and the input frequency or primary wave (A1), referred to as the ultrasonic parameter, is proposed to be used as an analytical descriptor of structural changes without interference of attenuation of the ultrasonic signal. Figure 4 highlights the strong correlation found between the nonlinear ultrasonic parameter and increasing flexural deformation of the PE specimen, most notable beyond the purely elastic limits (highlighted by the included dashed line). The initiation of plastic

behavior in the deforming specimen affects its crystalline network by creating residual stresses [12]. Higher harmonics are directed coupled with structural anisotropy induced by permanent spatial deformations [36,37].

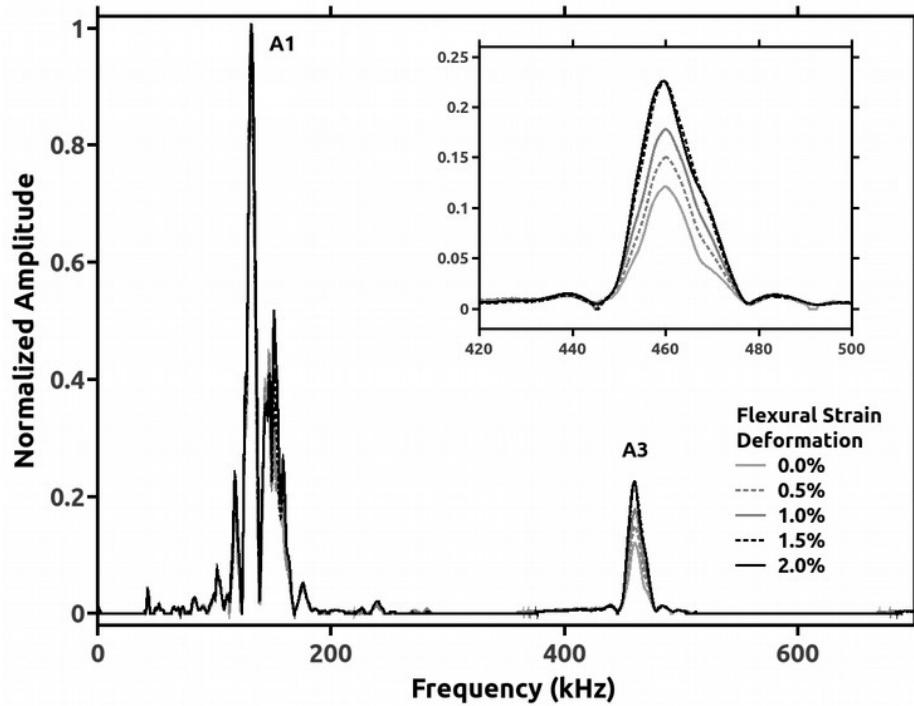
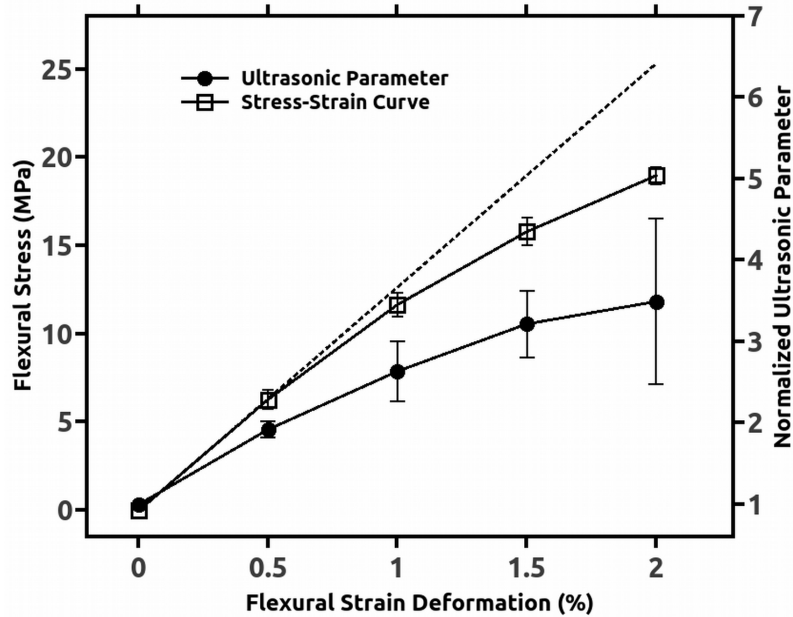
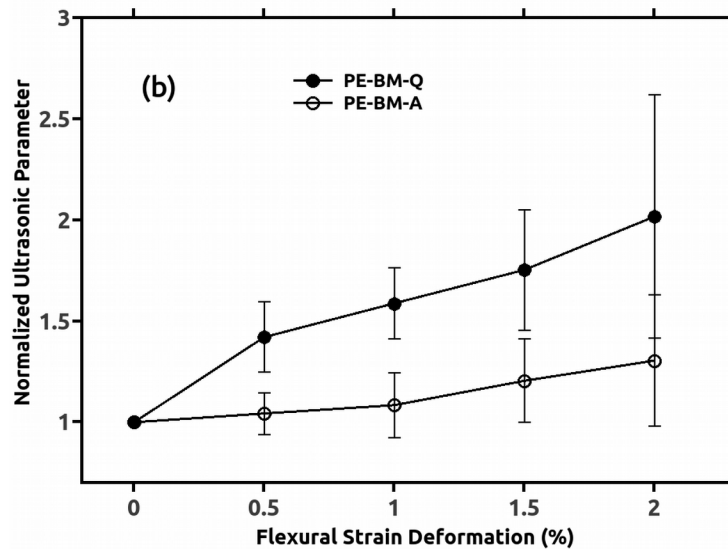
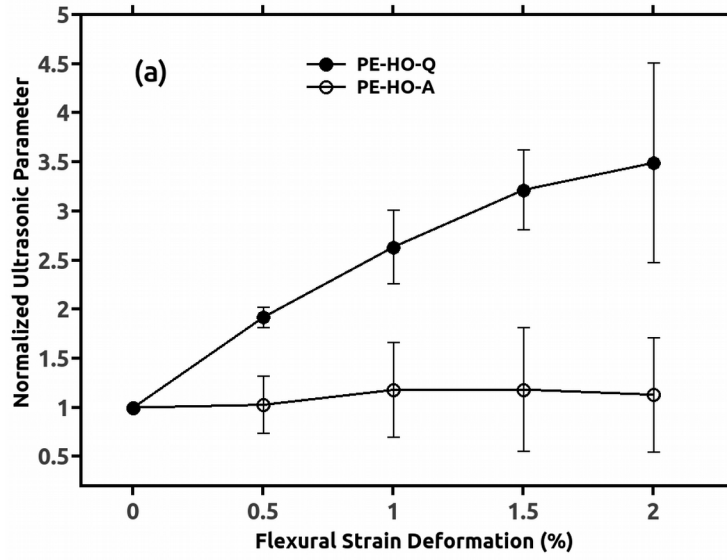


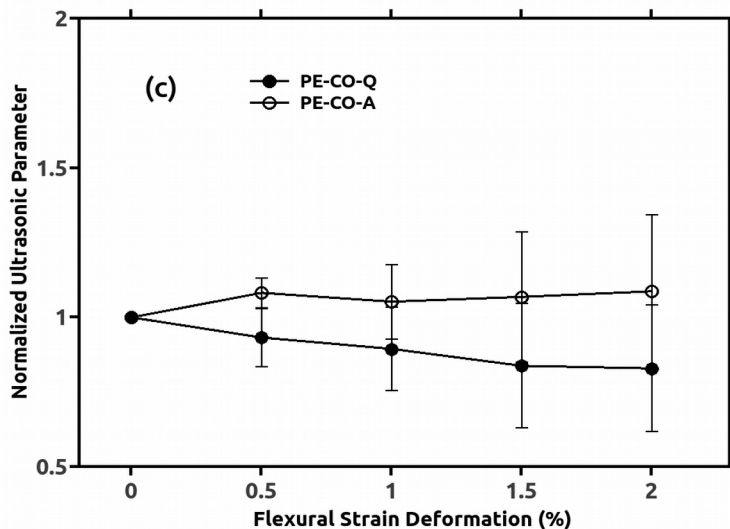
Figure 3 – Normalized ultrasonic frequency spectra for increasing flexural deformation in PE-BM-Q sample showing variation of third harmonic amplitude (A3) correlated with input frequency (A1)



**Figure 4 – Evolution of nonlinear ultrasonic parameter with increasing flexural deformation in PE-BM-Q samples (dashed and solid lines were included for visual reference only)**

Plots (a-c) in [Figure 5](#) show the profile of the ultrasonic parameter with increasing flexural deformation for samples with different thermal history. Samples with higher crystal content yet same quenched thermal treatment showed significantly higher values of the ultrasonic parameter with increasing deformation. Negligible change for the normalized ultrasonic parameter was observed for the annealed cases of both HO and BM, seen in plots (a,b), whereas their quenched cases showed a progressive increase with deformation. For CO, plot (c) shows the annealed sample produced the same lack of variation in the parameter seen with the other two resins, while the quenched sample increasingly exhibited a decrease in ultrasonic parameter value as deformation increased.





**Figure 5 – Profile of nonlinear ultrasonic parameter with increasing flexural deformation for homopolymer (a), bimodal (b) and copolymer (c) PE with different thermal treatments**

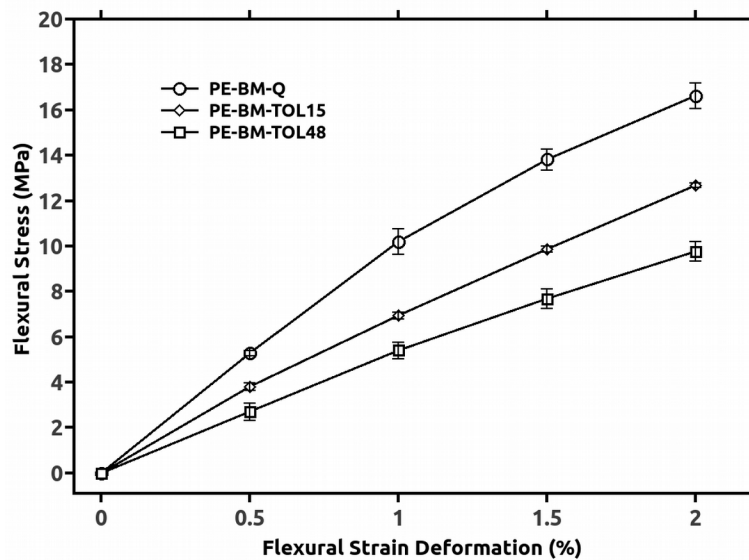
### 3.2. Effects of Swelling on PE properties

Effects of solvent swelling on incipient plastic behavior were examined with quenched BM and CO samples, which exhibited similar chemistries yet vastly different crystallinity. The changes in mechanical properties from long term immersion in toluene are reported in [Table 2](#). These two polyethylene grades are manufactured to enhance environmental stress cracking resistance, making them commercially interesting to study for exposure to solvents. A significant decrease is observed in the flexural modulus of both grades due to toluene penetration. This effect seen under flexural deformation is plotted in [Figure 6](#) for BM, which demonstrates a direct relation between declining modulus and the time allowed for penetration of toluene; the same trend was seen for CO and as a result, not shown in the figure. Although significant reduction of mechanical elastic properties was reported, no significant reduction in crystallinity was directly related to chemical swelling was observed in DSC tests for samples after 48 hours of contact with toluene. The absorption rate was significantly different with BM samples presenting an increase in weight of 2.1 % ( $\pm 0.1$ ) after 15 hours and 4.2 % ( $\pm 0.1$ ) after 48 hours of soaking; meanwhile CO samples had a higher weight gain with 3.1% ( $\pm 0.2$ ) after 15 hours and 6.0 % ( $\pm 0.3$ ) after 48 hours in contact with toluene. CO samples after

48 hours of contact with the fluid showed a significant increase in strain at break, demonstrating an expected plasticization effect of toluene [38]. Conversely, BM samples demonstrated an opposite effect, with a decrease in elongation before break, which was considered to similarly indicate a decrease in plasticity.

**Table 2 – Mechanical characterization for PE samples after chemical swelling**

Material	Flexural Modulus (MPa)	Tensile – Yield Stress (MPa)	Tensile – Elongation at break (%)
PE-BM-Q	1142 ± 85	25.4 ± 0.9	60 ± 37
PE-BM-TL48	617 ± 124	25.6 ± 0.3	35 ± 5
PE-CO-Q	749 ± 16	18.2 ± 0.2	197 ± 4
PE-CO-TL48	407 ± 23	18.9 ± 0.4	228 ± 32



**Figure 6 – Flexural stress-strain curves for bimodal (BM) PE samples with increasing swelling time**

Plots (a, b) in Figure 7 demonstrate how the signal amplitude (in the time domain) and ultrasonic parameter were affected by swelling for the quenched BM and CO samples. Attenuation of the average ultrasonic signal can be correlated with the effect of toluene to decrease elastic modulus, as shown in Table 2. However, the ultrasonic parameter, which is based on the nonlinear interaction with the structure of a material, did not follow the same trend. The harmonic amplitude ratio remained



insignificantly changed for BM, while progressively increased for CO based on contact time with the fluid.

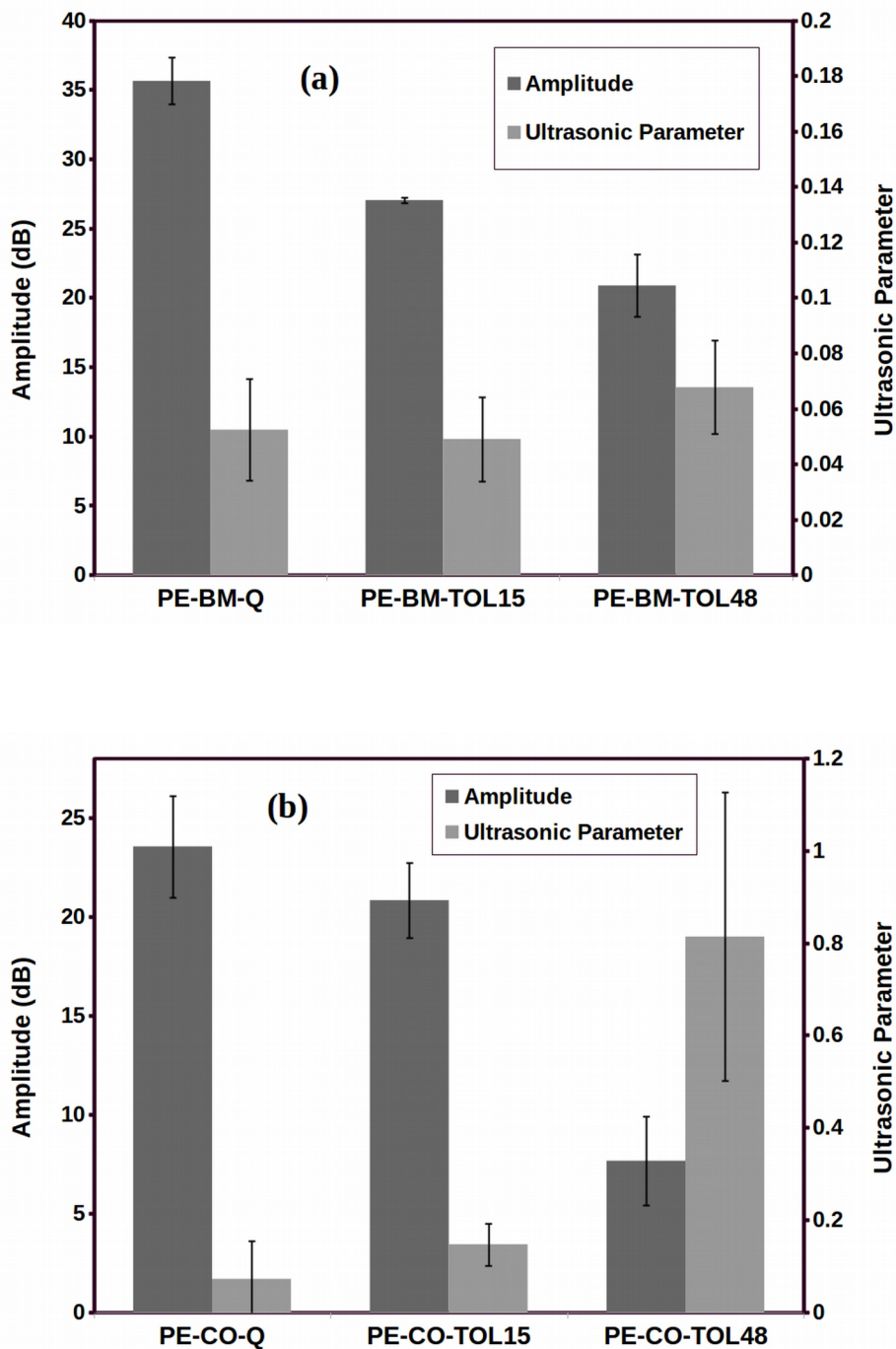


Figure 7 – Nonlinear ultrasonic parameter and the time domain signal amplitude for (a) bimodal and (b) copolymer PE with increasing time immersed in toluene

#### 4. Discussion

Results presented in the previous sections showed a distinctive elastic and plastic behavior among the PE samples studied. The three grades of polyethylene were chosen to highlight how the introduced ultrasonic technique can distinguish changing morphological details in the inter-crystalline region, often best detected by mechanical characterizations, that are related to incipient yielding and affected by annealing or swelling. The primary assumption of this study is that propagation of ultrasonic waves in PE will be dispersive and differ from a perfect elastic body. Therefore, our proposed approach focuses on the non-linear interaction of ultrasonic vibrations with the discontinuities of a semicrystalline network responsible for generating a signal with a frequency different than the original wave introduced [39]. Reliance on linear equations, such as Hooke's law, can only be applied to describe the bulk wave interaction through velocity and attenuation with major structural events, namely, cavitation and fibrillar transition [21,40,41]. The introduced nonlinear ultrasonic method is believed to be sensitive to more minute microstructure events that modify the crystalline network at incipient plastic deformation, by observation of the evolution of anharmonicity in PE samples with increasing stresses below the yield point.

Between quenched samples with differing crystal content it was observed that higher crystallinity promote a larger variation of the ultrasonic parameter for the same level of deformation. From Figure 5, while quenched HO and BM grades showed an increase of 2 to 3 times in the ultrasonic parameter after 2% of flexural strain was applied, CO quenched samples, with significantly lower crystallinity, demonstrated an actual decrease in the ultrasonic parameter from its baseline value for the same deformation level. There is casual relationship between the crystalline structure and differentiation of bulk PE from an ideal oscillator to small deformations [42]. However, comparison of ultrasonic parameter results from annealed to quenched samples showed that there is no direct correlation between the generation of harmonics and the degree of crystallinity. Noticeably, contributions to anharmonicity are not related to the size of PE crystals themselves, but on their

interaction through the non-crystalline regions.

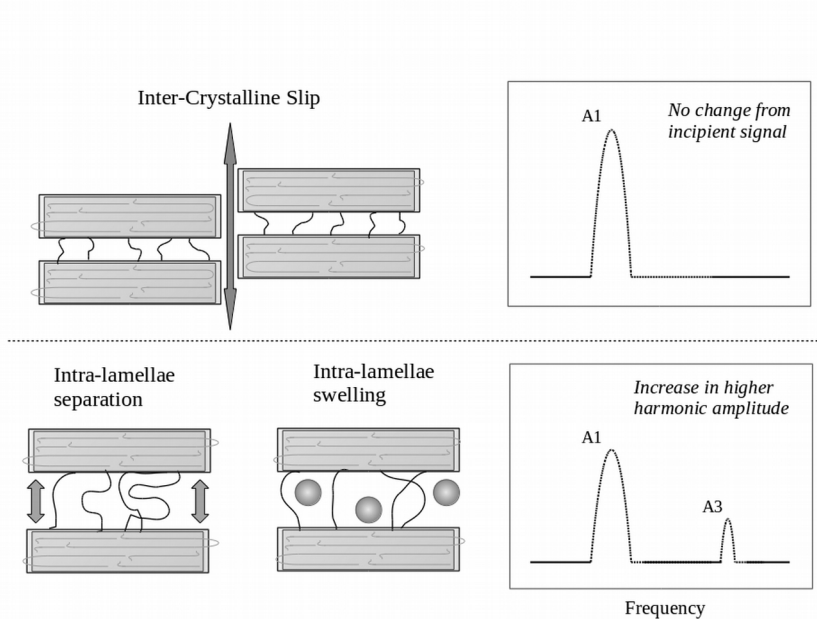
Three different mechanisms are normally used to explain initiation of plastic deformation: cavitation, elongation and shear [43]. For the PE grades tested under flexural load below yielding, no cavitation should be expected [44] leaving two competing crystallographic mechanisms to be considered, homogeneous crystal slip and heterogeneous lamellae stack separation. Both events occur in the vicinity of a inter-crystalline interface. In such cases, the density of tie chains plays a very important role in balancing between these two mechanisms. A reduction in plasticity is demonstrated through the significant reduction in elongation at break and slow crack growth time for annealed cases of HO and BM, reported in Table 1. The decline in these properties by annealing indicated a decrease in tie chains resulting from increasing lamellae thickness [34], which in part will favor inter-lamellae crystal slip during early stages of plastic deformation. From a bulk to meso-scale perspective, a higher concentration of crystal slips represents a homogeneous rearrangement of the macromolecular network for the same level of internal stresses [45], in this case induced by flexural deformation. Analysis of the ultrasonic parameter showed that samples with theoretically more homogeneous inter-crystalline dislocations caused by mechanical deformation presented little to no effect in the anharmonicity of the PE structure, while samples with expected higher concentration of heterogeneous intra-lamellae separation, ie. quenched HO and BM, showed an increase in the amplitude of higher harmonics. Nonlinear ultrasonic wave propagation can be correlated to microstructural asymmetries and discontinuities [25], thus relating the observed increase in ultrasonic parameter with plastic deformation through intra-lammellae separation that is expected to be prominent in crystals aligned to the applied force [13]. Conversely, it was the quenched samples rather than annealed case for CO that exhibited reduced slow crack growth time and elongation at break as well as produced significant attenuation of the higher harmonics, pointing to extensive occurrence of crystal slip in the former. The annealed CO samples showed the same resistance to variation of the ultrasonic parameter as the other

resins, which can be correlated with the reportedly hindering of the inter-lamellae slipping by secondary crystallization [46].

To complement the observations made by mechanical deformation, swelling results were presented as additional evidence on how the proposed ultrasonic test can be used to follow progressive changes in microstructure of polyethylene. Increased contact time of the samples with toluene showed a significant weight gain and reduction in the elastic modulus on both CO and BM samples. Penetration of compatible low molecular weight agents is expected to promote swelling on the amorphous phase, promoting separation of the crystalline lamellae stacks, which induce internal stresses within the intra-lamellae region [47]. Thus, observations of an increase in the ultrasonic parameter with exposure time to toluene might be interpreted as an indication of the level of penetration of the fluid, causing a reduction in mobility of the intra-lamellar region of crystallites closely located to the exposed surface. This hindering effect caused by the penetrating agent can be compared to the localized stress associated with heterogeneous dislocations in the highly crystalline quenched samples after incipient plastic deformation. A higher penetration rate was observed for CO samples, possibly due to its lower crystal content resulting in greater vulnerability to swelling [48]. And the stability presented by the BM can also be explained by the barrier effect of tie chains to diffusion of low molecular weight molecules [49]. These results highlight the potential of using the ultrasonic parameter to monitor diffusion of low molecular weight components over exposure time in polyethylene parts in use.

Based on the evidences shown in this study, nonlinear ultrasonics seems to be a relevant non-destructive method to characterize stress-induced micro-structural modifications of a crystalline network. This technique seems to have a potential to follow localized dislocations caused by stress concentrations in the intra-lamellae region related to incipient plastic deformation or swelling of low molecular weight penetrate, being insensitive to homogeneous deformation caused by inter-crystalline slip, as summarized in [Figure 8](#). Understanding early processes of plastic deformation can help predict

the kinetic control over the propagation of dislocations in the later stages [50]. Further theoretical analysis and modeling can also help understand the capabilities of this method to quantify and predict the long-term plastic behavior of tested samples in operating conditions [51]. However, it is also important to highlight that propagation of the ultrasonic guided waves in the bulk material is affected by several characteristic properties. Thus, the path to a practical application of this technique requires the possibility of isolate the micro-structural phenomena from other macroscopic changes that might affect the signal, such as reducing dimensional and surface changes.



**Figure 8 – Schematic of the correlation between plastic deformation and swelling of PE samples with increase in higher harmonic amplitude of ultrasonic guided waves**

## 5. Conclusions

Plasticity of PE samples with different thermal history and after chemical swelling was evaluated using traditional destructive methods and a proposed non-destructive alternative using ultrasonics. A nonlinear ultrasonic parameter, based on the the amplitude ratio of the third harmonic and the input frequency, was correlated with increased heterogeneous dislocations and swelling in the

intra-lamellae regions. Results showed that the proposed method was able to monitor microstructural changes in crystalline network during incipient plastically deformed PE samples from different grades and thermal history. Variation of the ultrasonic parameter with increasing flexural deformation was stronger for samples with crystalline morphology that favor intra-lamellae separation over inter-crystalline slip.

Annealed samples for HO and BM grades showed a reduction in plasticity, observed from traditional destructive short-term and long-term tests and also through a significant reduction in the variation of the ultrasonic parameter. Changes can be linked to a significant reduction in the concentration of tie chains due to the thermal treatment. Secondary crystallization observed in annealed CO samples caused an opposite effect, with a hindering effect comparing results from quenched CO samples. A second observation of application of the proposed method to monitor changes to the inter-lamellae region was demonstrated by the lower variation of ultrasonic parameter and sorption of toluene in BM over CO samples subjected to the same contact time, highlighting different barrier properties due to crystalline morphology and plasticity.

Different from the traditional ultrasonic testing that can mostly be linked with variations of elastic properties or dimensional changes for PE samples, this proposed approach based can provide important quantification of the contribution of different semicrystalline morphologies to the resistance to plastic deformation. With further research and development this method can become an important nondestructive technique for characterization of PE.

### **Acknowledgments**

Special thanks for Ron Cooke and Mark Woolston for the technical support and material. Also the funding support by Imperial Oil Ltd and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) - Brazil through the Science Without Borders Scholarship Program.

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