

Viscoelastic Characterization of Fusion Processing in Bimodal Polyethylene Blends

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ABSTRACT

Polyethylene is an advantageous material for the construction of buried pipelines. It is corrosion resistant, seismic tolerant, and utilizes low cost installation methods. Pipe sections are often joined using thermal fusion processes. The strength of the joint is related to the ability of the polyethylene chains to inter-diffuse and form inter-crystalline tie-chains across the two polyethylene surfaces. Testing the strength of the fusion bond is difficult and a number of different destructive and non-destructive tests have been developed, but it is not possible to understand the impact of the fusion process on the local microstructure from these tests. In this work, instrumented indentation with a flat punch is used to measure the local viscoelastic behavior of five different polyethylene resins used for pipe manufacturing at short times. High strain behavior related to slow crack growth is measured using a strain hardening measurement under tension. The impact of thermal processing is investigated by imposing three different thermal cooling histories (0.4 °C/min, 9 °C/min, and 100 °C/min) on the polyethylenes. The goal is to determine if short-term creep under indentation is capable of accurately measuring; a) bulk creep behavior, b) impact of resin architecture, and c) the impact of thermal processing. The results show that indentation using a flat punch is capable of measuring creep within the range of bulk creep behavior, but not sensitive to the slow crack growth resistance of the resin.

KEYWORDS indentation, polyethylene, slow crack growth, creep, fusion bond

INTRODUCTION

Polyethylene (PE) is important for critical infrastructure applications such as drinking water, waste water, and fossil fuels transportation. The advantages of polyethylene are competitive cost compared to metallic pipe, lower corrosion rates, and toughness. Central to the durability of polyethylene is not only its low reactivity with the environment, but also the microstructure of the material. Slow crack growth (SCG) is the predominant long-time failure mode for these materials. The process of SCG failure is understood as a stress concentrator, such as a contamination, catalyst particle, or damage in the pipe causes small voids to form a small crack in the pipe. These voids grow and form craze fibrils ahead of the stress concentration. The craze fibrils grow in length as the polyethylene chains disentangle from each other and the crystalline lamellae break up locally. The crack advances when the craze fibril breaks and stress shifts to the remaining fibrils, which causes them to break. Eventually the pipe fails in a brittle, rather than ductile, manner. This process is a creep driven failure and largely controlled by the tie-chains present in the pipe material [1].

Early pipe technologies utilized a single molecular weight distribution with short chain branching (SCB) to reduce SCG failures. Short chain branching along the backbone of the main polymer encourages the formation of tie-chains and increases entanglements within the amorphous region of the polyethylene. High performance resins used for piping applications are composed of a bimodal blend of two different polyethylene molecular masses: a medium to high density linear chain and a medium density branched chain (< 10 branches per 1000 monomers). The advantage of the bimodal distribution is that the linear chains crystallize to provide the pipe its strength, while the branched chains resist chain pull-out giving the material exceptional slow crack growth resistance [1]. The SCG failure of polyethylene resins is sensitive to the microstructure of the resin, which depends on the polymer as well as the flow and thermal history during processing. For example, Ting and coworkers have shown that bimodal formulations require higher force to initiate failure and have higher ultimate failure strains than unimodal resins [2]. In the case of a fusion bond, which is often used to join pipe segments, the polymer is the same, but the thermal and flow history in the joint region can change local properties so they differ from those of the parent

pipe. The heat affected zone (HAZ) may have altered crystallinity, molecular orientation and, in the case of the bimodal system, changes in composition.

Recently, the nuclear industry has been interested in the application of greater than 1 m diameter pipe for water transportation. While the structure-property relationships for pipe are generally understood, less is known about long term performance of thick walled pipe, particularly the fusion joints used to join these pipe sections. There has been concern that standard test methods for fusion joints do not adequately predict failure time for SCG [3]. In the past few years, the Welding Institute (TWI) in the U.K. has developed a whole pipe creep rupture test that is uniquely suited for long term failure measurements of fusion joints [4]. A challenge for any full pipe based test method is the cost required for evaluating large diameter pipe fusion joints. It would be advantageous to develop a coupon level metrology for conducting design of experiments and sensitivity analysis prior to testing large diameter pipes. The current research program at the National Institute of Standards and Technology (NIST) aims to develop an understanding of the viscoelastic and viscoplastic behaviors for PE resin materials as a function of temperature, pressure, and cooling profiles observed during the formation of butt fusion joints in polyethylene. The initial focus is the heat affected zone (HAZ) around the fusion. Instrumented indentation is investigated as a metrology to quantify the local viscoelasticity across the HAZ zone and into the fusion bond. If instrumented indentation is capable of measuring the local viscoelasticity of the polyethylene and this behavior connected to the local microstructure of the polyethylene; this would provide an experimental route to maximize fusion bond conditions and provide the mechanical framework for modeling these thermal joints.

EXPERIMENTAL DETAILS

Five different PE resins (DOW) were measured for this work⁴. One was a unimodal resin which has a Pennsylvania Edge Notch Test (PENT) (ASTM F1473) value of ~ 200 hours; while the other four were bimodal resins with PENT times from greater than 5000 hours to greater than 15000 hours as shown in Table 1.

Table 1. Properties of the 5 different polyethylene resins

		PE-U	PEb-1	PEb-2	PEb-3	PEb-4
		Unimodal	Bimodal	Bimodal	Bimodal	Bimodal
Density (g/cm ³)		0.946	0.949	0.949	0.949	0.941
Melt Index (g/10 min)	190°C/2.16 kg	0.1	0.08	0.08	0.06	
	190°C/21.6 kg	8.3	8.5	7.0	5.5	9.5
Tensile Elongation (%)		850	>500	>500	>500	>600
Slow crack growth (hr)		200	>5k	>10k	>10k	>15k
Flexural modulus (psi)		120k	150k	150k	150k	>90k
Tensile strength (psi)		3200	>3500	>3500	>3500	>2600

Each resin was compression molded into a 15 cm x 15 cm x 500 μm plaque at 160 °C according to a procedure described in [7]. After pressing, the samples were removed from the press and placed in between two brass platens and manually clamped at all edges using C-clamps. The samples were reheated to 160 °C in an oven and cooled using either controlled cooling (0.4 °C/min and 9 °C/min) or quenched in an ice water bath (> 400 °C/min). The effect of thermal processing on the crystallinity, melting temperature, and lamellae thickness was characterized using Differential Scanning Calorimetry (DSC) scanning from room temperature to 160 °C at 10 °C/min. The lamellar thickness was calculated using the Gibbs-Thomson equation [6].

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_m l} \right) \quad (2)$$

where T_m is the measured melting temperature, T_m^0 is the equilibrium melting point of an infinite crystal (415 K), σ_e is the surface free energy of the basal plane ($60.9 \times 10^3 \text{ J/m}^2$), and Δh_m is the enthalpy of fusion per unit volume ($2.88 \times 10^8 \text{ J/m}^3$), l is the lamellar crystal thickness.

Bulk creep of selected resins was measured in tension using 10 mm x 10 mm rectangular bars. An initial stress of 2.75 MPa was applied to the bar at time equal to zero. The resulting change in strain from 0.17 % to 0.51 % was measured over the 10,000 s. The creep compliance was calculated as a function of change in displacement with time.

In order to determine whether the thermal treatment impacted the SCG resistance of the resins, the SCG resistance was measured using a strain hardening (SH) technique [7,8] conducted at 80 °C. In order to correlate with the indentation

measurements, the strain hardening modulus was measured at room temperature. The strain hardening modulus was measured as the slope of the stress vs. strain curve, ($\langle G_p \rangle$), after the polyethylene natural draw ratio between an extension ratio of 8 to 12. The current study uses SH measurements of dog bone samples (ASTM D-638). The tests were performed at a constant displacement rate of 10 mm/min [7,8] using an electromechanical test machine (Instron) and laser extensometer to measure strain. Prior to SH testing, the specimens were allowed to equilibrate at 80 °C in the oven for 30 min. A minimum of three tests were run for each type of specimen.

The creep behavior of the resins was measured using instrumented indentation with a 50 μm flat punch indenter over 600 s following the method of Herbert [9]. In this method a large step load ($P_1=50$ mN) is applied to the sample to achieve conformal contact with the flat punch. An iterative control loop holds the load constant while measuring the displacement over time. The loop calculates whether the slope of displacement over time is below a drift threshold of 0.3 nm/s, in this case. If the tip has significantly drifted, then the controller moves the tip back to the original displacement in the sample and holds the new load, P_2 , for another iterative round. Once the drift threshold has been met the indenter applies a smaller load and the displacement as a function of time is measured under this constant P_2 . The creep under three different constant loads of 3 mN, 6 mN, and 9 mN was investigated. In the time domain for instrumented indentation experiments the creep compliance using a flat punch may be calculated from equation (1) [10].

$$J_c(t) = \frac{2Rh(t)}{P(1 - \nu^2)} \quad (1)$$

where $J_c(t)$ is the creep compliance, R is the radius of the flat punch, $h(t)$ is the displacement time response, P is the applied constant load, and ν is the time independent Poisson's ratio ($= 0.35$).

RESULTS AND DISCUSSIONS

The morphological characteristics within polyethylene are important for the ultimate properties of the material. The SCG behavior of polyethylene is a function of the molecular weight distribution, the amount of short chain branching and the distribution of the short chain branches. The crystalline lamellae provide the strength for the material, but the chains that cross the amorphous regions to form tie chains increase the yield strength. The harder it is to disentangle those chains in the amorphous region, through the presence of short chain branching, the better the SCG resistance of the material. Slowing the speed of the material through the crystallization transition can increase the amount of order within the system, which may allow for the formation of larger crystals and less amorphous region. Quenching the material will decrease the order within the system, which will decrease the size of the crystalline lamellae and increase the amount of amorphous material. The question of whether cooling rate will change SCG resistance is difficult to establish for a broad range of molecular weight distributions since the formation of tie chains is not directly correlated to % crystallinity (%X) or lamellar thickness [11]. Sardashanti [12] has shown that accelerating the cooling rate decreases the % crystallinity and decreased the lamellar thickness. The authors also reported that decreasing the cooling rate slightly decreased the corrected strain hardening modulus for several polyethylenes. This was indicative of worse SCG performance for the resins the slower the cooling rate of the material.

The thermal measurements from the DSC show that decreasing the cooling rate does not induce a significant change in the % crystallinity within the sample. It does increase the melting temperature. Figure 1 shows the lamellar thickness change for the polyethylene resins as a function of cooling rate. Decreasing the cooling rate shows an increase in the lamellar thickness. The increase in lamellar thickness is greatest for the bimodal materials compared to the unimodal polyethylene. While there is a difference between the lamellar thickness of the unimodal and the bimodal materials for all cooling rates, there is no significant difference between the different bimodal polyethylenes (PEb-1 to PEb-4). The increase in lamellar thickness suggests that increasing the cooling rate might decrease the SCG resistance. The strain hardening modulus was measured in order to estimate the changes in the SCG resistance for these materials.

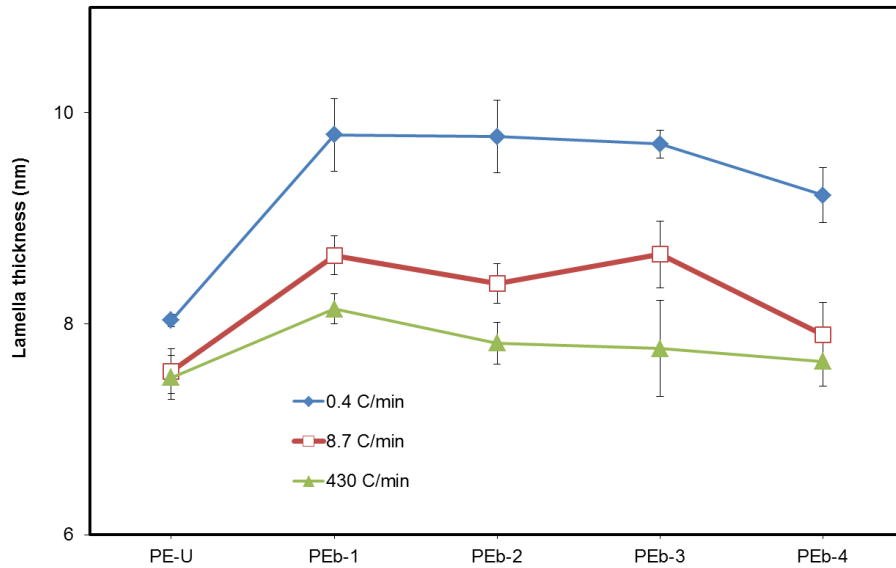


Figure 1. Lamellar thickness of the polyethylene resins, calculated from equation (1), as a function of different cooling rates.

The strain hardening modulus ($\langle G_p \rangle$) at 80 °C was 33 ± 3 for the unimodal material and 48 ± 4 for the bimodal materials. These values agree with those found in the literature [7,8,11,12] and show that this technique is able to measure differences between materials with large differences in $\langle G_p \rangle$ and PENT values. The strain hardening method was not able to discern differences between the bimodal materials. These materials only exhibit a difference in PENT failure time of a factor of 3 compared to a difference factor of ~ 30 for the unimodal. The strain hardening modulus did not change significantly with thermal treatment for any of the polyethylene materials. This suggests that the strain hardening modulus is not significantly impacted by cooling rate for these polyethylene materials. If the strain hardening modulus is a corollary for SCG resistance, then this suggests the SCG resistance of the polyethylene is not affected by cooling rate. Fracture tests are currently under way at NIST to verify that conclusion, but it may be that this technique is not sensitive in the strain hardening range of these high performance resins. The cooling rate does have an effect on the lamellar thickness and melting temperature of the polyethylenes, but it is not a large enough effect to alter the tie-chain structure within the material. This suggests that creep measurements of the materials should not be affected by the cooling rate either.

Figure 2 shows the creep compliance measured with instrumented indentation on the unimodal polyethylene, PE-U, under a 6 mN load. This figure shows the creep compliance for the complete load-hold segment. A transparent red rectangle has been placed on the figure to represent compliance data that would be affected by the load step. The size of this box is based on the convention that 10x the loading time should be given for the material to relax the P_2 load step. In this figure the different cooling rates lay over the top of each other. The curve has a slight curvature on the log-log scale with curvature increasing at long times. The magnitude of the creep compliance measured from indentation is slightly higher than bulk measurements for this material. Bulk tension creep measurements (not shown) indicate that creep compliance starts at $6.0 \times 10^{-10} \text{ m}^2/\text{N}$ and increases to $1.0 \times 10^{-9} \text{ m}^2/\text{N}$ over 600s. This is lower than the instrumented indentation measurements and may reflect the differences in the loading methods.

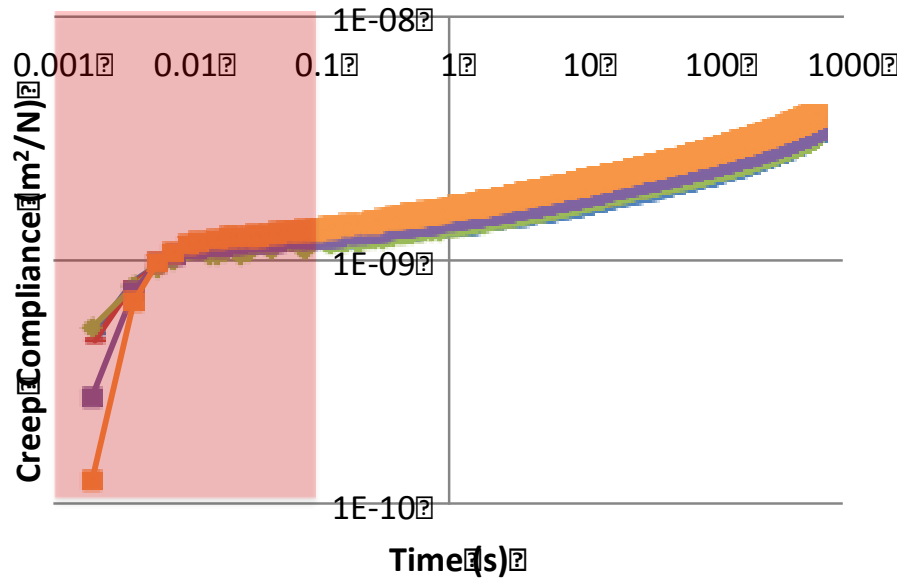


Figure 2. $J(t)$ measured for the PE-U sample using a 50 μm flat punch indenter at creep loads of 3 mN, 6 mN and 9 mN.

CONCLUSION

The impact of cooling rate on the microstructure, strain hardening, and creep behavior of five different polyethylene pipe materials was investigated. It was found that increasing the cooling rate does not significantly change the % crystallinity, but does reduce the order in the system. This was characterized through the melting temperature and lamella crystal thickness. The high strain behavior of the materials was characterized using strain hardening, which has been shown to correlate to SCG resistance. Strain hardening measurements showed a difference between the unimodal and bimodal materials, but could not discern the differences in the SCG resistance of the four bimodal resins. This technique did not measure a difference in the strain hardening modulus as a function of cooling rate either. The viscoelasticity of the materials was characterized using both small-strain bulk creep and instrumented indentation creep. The bulk and indentation measured creep differed, but were within a decade of each other for compliance. The source of error between these two techniques is under investigation. Both the instrumented indentation and the strain hardening measurements show for PE-U that the cooling rate didn't significantly affect the viscoelastic behavior of the polyethylene resin.

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