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Test Method

Alternative accelerated and short-term methods for evaluating slow crack growth in polyethylene resins with high crack resistance

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ABSTRACT

The current market has widely adopted the new polyethylene pipe grade PE 100 RC (resistant to cracks) for pipe applications. However, the main drawback of this material is the long test period (~10,000 h) required for ranking the resins. This paper proposes a modified Pennsylvania edge-notch tensile (PENT) test with higher load and temperature conditions (2.8 MPa and 90 °C). With the modified PENT test, failure time is six times shorter but slow crack growth is maintained. Additionally, it evaluates and finds an unexpected relationship between the strain hardening modulus and specimen thickness. These results suggest that the 0.30-mm thickness recommended by ISO 18488 is not optimal. Therefore, thicker specimens are proposed for accurate strain hardening modulus determination. Both methods are viable alternatives for evaluating the failure resistance of the new polyethylene pipe grades.

1. Introduction

Slow crack growth (SCG) is a key failure mode affecting polyethylene (PE) pipes. Under a relatively low stress level and after a certain amount of time, polyethylene pipes suffer a specific brittle failure, progressing from craze formation to subsequent propagation and ending in material failure [1,2]. However, the introduction of bimodal and multimodal polyethylene resins, with a comonomer distribution in the high molecular weight region, has considerably improved the SCG resistance [3–5]. These new resins are more resistant to stress cracking because of recent modifications and improvements, especially with the introduction to the market of the high-resistance polyethylene grade PE 100 RC. However, this significant technological advancement presents challenges for conventional long-term SCG determination tests. SCG failure times have increased dramatically up to values of around 10,000 h (almost one year) when using common tests such as the full notch creep test (FNCT), Pennsylvania edge-notch tensile (PENT) test, notch pipe test (NPT), and point loading test (PLT). With such a long time span, the thermal-ageing effect may seriously influence the resin failure process, preventing slow crack growth from controlling the failure mechanism. Therefore, alternative test methods that speed up the standard long-term methods should be sought for evaluating slow crack growth, while ensuring that brittle failure, not ductile failure or thermal ageing, controls the failure mechanism.

Newly developed alternative methods reduce the long failure times in evaluating SCG resistance by modifying test parameters (e.g., geometry, stress, and temperature) and thus accelerating the assay [6]. The standard conditions for the PENT test are 2.4 MPa and 80 °C. We proposed modifying certain PENT test parameters to speed up the determination of stress-cracking resistance. Depending on the applied stress (σ), the polyethylene resins may experience brittle, ductile, or mixed failure. Brittle failure belongs to the region below the critical stress value (σ_c), where the material fails following slow crack growth. Slow crack growth is a thermally active process, and the failure time is generally reduced when the temperature is increased. It is necessary to find the optimal temperature conditions (above 80 °C to accelerate failure time) and degree of stress under which the failure is still brittle. We thoroughly studied all of these factors in a previous work [7], and the results suggested that a temperature increase up to 90 °C prompted the brittle failure mechanism, similar to that obtained for 80 °C. Additionally, a more severe loading condition of 2.8 MPa led to an SCG process under the brittle failure mode but significantly

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reduced the failure time. The failure surfaces were tested at different temperatures to confirm whether, under these conditions, the main failure mechanism was still slow crack growth. With modified parameters, failure time is six times shorter than with the standard conditions defined by the ASTM F1473 PENT test. However, at least two months are needed to ascertain the slow crack growth of some resins.

In recent years, methods such as the natural draw ratio (NDR) [8–10] and the strain hardening (SH) modulus (<G_p>) have been developed based on short-term mechanical properties. The main advantage of both methods is that they significantly reduce the stress crack resistance evaluation time to a few hours. Both methods were correlated with the failure time according to standard SCG tests, such as PENT, FNCT and environmental stress crack resistance (ESCR). However, several works reported that the strain hardening modulus correlates better with the PENT test than with the NDR [11]. The strain hardening modulus methodology (ISO 18488) analyses the last part of the stress–strain curve further above the natural draw ratio region [12] to simulate the fibrillar condition developed in craze formation [13–15]. This procedure correlates well with SCG tests (e.g., FNCT or PENT), and is thus a feasible method for ranking materials according to their short-term SCG performance, while using a small amount of material [16]. The strain hardening modulus method has gained acceptance by the scientific community and companies, with many research groups studying the approach [17–20] and extending its use to other pipe materials, such as polypropylene [19].

This study evaluates slow crack growth using the PENT test, a standard SCG test reported in ASTM F1473. However, this is a modified PENT test: the influential parameters of applied stress and temperature were changed in order to quickly evaluate stress-cracking resistance but without altering the brittle failure mechanism characteristic of slow crack growth. The SCG evaluation time was six times shorter with the modified PENT test. In addition, the strain hardening modulus was evaluated as an alternative to conventional long-term methods, but again we modified several physical variables to determine the best experimental conditions and correlations with conventional SCG tests. Thus, the strain rate and specimen thickness were compared with the standard parameters adopted by ISO 18488. Both variables were proved to significantly influence the strain hardening modulus value determination; therefore, the specimen thickness recommended by ISO 18488 is not the optimal value.

2. Experimental

2.1. Materials

This work studied 14 commercial PE 80, PE 100, and PE 100 + polyethylene grades, all of which were ethylene-1-butene copolymers based on a Ziegler–Natta catalyst and with bimodal molecular weight distribution.

2.2. Pennsylvania edge-notch tensile (PENT) tests

To perform the PENT tests, 10-mm-thick plaques were compression-moulded in a hydraulic press at 180 °C with a nominal pressure of 200 bars. Afterwards, they were cooled slowly for 5 h at a rate of approximately 0.5 °C/min until reaching room temperature. During the cooling stage, the pressure was decreased naturally in accordance with ASTM F1473. Specimens of 50 × 25 × 10 mm were machined from the plaques, followed by notches slowly pressed into the specimen by a razor blade at a speed of about 200 μm/min. Side notches of 1.0 mm and a front notch of 3.5 mm were made according to ASTM F1473.

This study evaluated the standard PENT test and a modified PENT test. The standard PENT test was developed by Norman Brown et al. [21] and later standardised in ASTM F1473 and ISO 16241; its established conditions are 2.4 MPa and 80 °C. For the modified PENT test proposed by our group [7], the conditions were 2.8 MPa and 90 °C.

2.3. Strain hardening modulus determination

The strain hardening modulus is easily determined from a simple uniaxial tensile test at 80 °C and was performed according to ISO 18488. The test was performed in a universal testing machine (INSTRON 5565) with a 500 N load cell, and the elongation was determined using a video extensometer (INSTRON 2663–822). The samples were compression-moulded to a sheet with a hydraulic press at 180 °C and a nominal pressure of 200 bars, and the cooling rate was 15 °C/min, as per ISO 1872–2. After pressing, the samples were annealed for 1 h at 120 °C and then slowly cooled to room temperature. Dumbbell-shaped specimens were punched from the pressed sheets, and the initial distance between the gauge marks on the centre of the test specimen was approximately 12.5 ± 0.1 mm. Two sheets were pressed, one 0.30 + 0.05/-0.03 mm thick (ISO 18488) and the other 2.0 ± 0.1 mm thick. The laboratory device used to measure the thickness had the required accuracy (0.005 mm). This device is usually controlled using certified calibration standards in the range of the thicknesses studied. According to ISO 18488, the strain rate is 20 mm min^{-1}, but for this study we applied two additional strain rates, 3 mm min^{-1} and 10 mm min^{-1}. For some polymers, we also tested specimens with additional thickness values.

2.4. WAXS measurements

We obtained wide-angle X-ray scattering (WAXS) diffractograms of the samples at room temperature using a Bruker Microstar rotating-anode generator with a copper target. WAXS patterns were recorded using a Mar345 dtb image plate with a resolution of 3450 × 3450 pixels and 100 μm/pixel, using a sample-to-detector distance of 200 mm. The experimental data were corrected for X-ray absorption and background scattering. The patterns were analysed using FIT2D software.

3. Results and discussion

3.1. Modified PENT test

Four principal variables influence the PENT test: specimen geometry, notch depth, load and temperature. In this study, we did not modify geometry and notch depth, because they were the focus of previous studies and were necessary to maintain the plane-strain conditions that favour brittle failure. However, we did modify applied stress and temperature and then studied the results for the 14 polyethylene grades.

All polyethylene resins underwent the standard PENT test (2.4 MPa, 80 °C) and the modified PENT test (2.8 MPa, 90 °C). Fig. 1 shows a good linear fit between both tests for a wide range of materials, from PE 80 to PE 100+. The sample failure times ranged from 20 to 8000 h using the standard PENT test. Using the modified PENT test, the stress-cracking failure times for all resins were six times shorter. In all cases, the fracture surfaces showed a fibrillar morphology in which slow crack growth is the dominant process. Thus, the ageing or melting processes are negligible, and the failure mechanism is ruled by slow crack growth, at least up to the maximum failure time obtained (8000 h at 80 °C and 1500 h at 90 °C). Table 1 summarises the results according to the time