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Test Method

On the relevance of a notch creep test for the comprehension and prediction of slow crack growth in PVDF

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Abstract

Modeling slow crack growth (SCG) in polyvinylidene fluoride (PVDF) needs shorter tests than the burst resistance tests usually performed on pipes. In this paper, creep experiments were performed on three-notched extruded and compression-molded specimens. Two distinct regimes were indicated from the kinetics of crack opening displacement (COD). At high temperatures and low stresses, the COD rate decreases until reaching a steady-state stage from which stress sensitivity and activation energy were determined. Investigations of the damage morphology by scanning electronic microscopy (SEM) revealed that the steady-state stage actually corresponded to the process zone thickening. Unlike in polyethylene, the process zone length could not be deduced from the COD measurement and the crack propagation kinetics could not be predicted. Nevertheless, this kind of test appears relevant to indicate the creep resistance of fibrils ahead of the crack tip, which remained a key mechanism in SCG in PVDF also, to predict more rapidly its stress sensitivity and to discriminate materials.

Keywords: Polyvinylidene fluoride; Slow crack growth; Crack opening displacement; Process zone; Cavitation; Pipes

1. Introduction

Like high-density polyethylene (HDPE), apolar polyvinylidene fluoride (PVDF) has been one of the semi-crystalline polymers widely used for years for long-term pressurized pipes applications. PVDF pipes, mainly involved in chemical applications, are usually designed from standardized burst resistance tests [1]: pipes are submitted to constant temperature and internal pressure and the average hoop stress (calculated from the internal pressure in an elastic thin pipe framework) is plotted against lifetime (measured at pipe leaking) on a log–log scale. Both HDPE and PVDF pipes undergoing constant pressure at high temperature display two distinct failure modes. Under average hoop stress higher than a critical value σ_c, pipes fail in a ductile mode due to localization of the deformation and creation of a blister. The ductile regime is rather well known now in both HDPE [2] and PVDF [3–5]. Previous works on PVDF addressed micro-mechanisms

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involved in the bulk [3] or ahead of a crack tip, [4] as well as damage modeling in the bulk [4]. The ductile regime is governed by widely spread cavitation and generalized plasticity. This leads to rather short lifetimes. The relationship between average hoop stress and lifetime follows a power law:

$$\sigma = Ct^{-1/n}, \quad (1)$$

where n is a stress sensitivity parameter and C a constant parameter.

Unfortunately, any extrapolation of this average hoop stress vs. lifetime curve towards the long-term behavior under stresses below σ_c is prevented by the onset of a drastically different failure mode appearing at low pressure and high temperature. This regime is characterized by the slow and localized propagation of a very small crack through the pipe wall. Although it is sometimes called "brittle" because no macroscopic plastic deformation is observed near the fracture zone, less ambiguous terms like "low stress regime" or "slow crack growth regime" (SCG) will be preferred in this paper. In this SCG regime, the average hoop stress can be expressed again by Eq. (1), the stress sensitivity factor n being much lower than in the ductile regime. Previous optical and electronic microscopy observations in PVDF [6] allowed both the characterization of cracks morphology in the SCG regime and the understanding of how cracks nucleate and propagate. A porous zone was shown to nucleate within the pipe wall, just below the inner skin. Micro cracks further propagated both through the thickness and along the pipe axis, emerging at the inner surface first. Due to the pressurized water penetrating the crack, the last stage of propagation was thought to be short before emerging at the outer surface of the pipe.

A major concern for predicting pipe durability arises from the onset of the SCG regime: accelerated tests are needed to activate the SCG micro mechanisms within shorter times than generally involved in classical burst resistance tests (several months at least). Micro mechanisms actually activated in the accelerated test need to be specified and compared to that observed in the pipe to ensure the relevance of the short-term test.

Among the numerous short-term tests aimed at investigating SCG behavior in PE, the PENT test developed by Brown et al. [7] was based on the creep of three-notched specimens. Such a non-symmetrical geometry ensured propagation conditions very close to that in the pipe wall. Time evolution of the crack opening displacement (COD) was measured at the notch roots. A damaged process zone—fibrillar near the crack tip and porous far from it—was evidenced in PE and was shown to follow a two-stage process: an incubation stage, characterized by a constant COD rate, and an actual propagation stage, characterized by the fracture of successive fibrils rows and leading to fracture. Most studies focused on the steady-state stage and on either the stress or the temperature sensitivity of the COD rate. This sensitivity was found equal to that of the propagation stage [8]. Therefore, it enabled prediction of crack propagation kinetics from the incubation stage. Since the damaged zone remained triangular with constant angle throughout the test, the propagation kinetics could be easily deduced from the COD measurement [9,10].

Alternative tests were developed as well to discriminate materials and optimize molecular design. Various sample geometry—mainly cylindrical notched bars or four-notched parallelepiped samples—were tested in static [11,12] or fatigue conditions [13–15]. Since mechanisms and kinetics of fibril creation and extension were of major importance, some tests were dedicated to the creep behavior of the oriented polymer after necking [16–18] and further used to indicate micro structural effects e.g. molecular mass distribution, tie molecule density, size of crystalline domains for homopolymers or lateral branches density for copolymers [11,12,14,16–23]. Continuous networks made of tie molecules and crystals exhibited a better resistance to SCG propagation. Mechanical loading effects were investigated as well [23]. The natural draw ratio measured from uniaxial tensile tests appeared to be a relevant and discriminating indicator for the long-term cracking behavior of PE-based materials [17,18].

This paper aims to apply a short-term test to apolar PVDF to highlight its SCG mechanisms at high temperature. The relevance of the chosen accelerated test for predicting SCG kinetics in PVDF will be examined, comparing the damage morphology to that observed in burst resistance tests [6].

2. Experimental

2.1. Materials

Commercial grade (Kynar 740®) alpha-PVDF (monomer CH_2–CF_2) was supplied by Arkema. It is a linear homopolymer displaying a glass transition