Mechanical Properties Study of HDPE Wall Pipes Exposed to Sulfuric Acid and Toluene-Methanol Mixture: Comparison Between Filament and Standard Specimens

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Résumé:
Dans cette communication, les résultats de deux études expérimentales sont présentés et comparés. Ils concernent l’évolution des propriétés mécaniques à travers la paroi d’un tube HDPE utilisé pour le transport du gaz naturel. Dans la première étude, des éprouvettes filaments (ISO 3341) usinées sous la forme de copeaux uniformes et continus sont utilisées alors que la seconde utilise des éprouvettes standards selon ISO 527. Les deux approches ont permis de montrer qu’il y a une variation importante des propriétés mécaniques à travers la paroi du tube en allant de l’extérieur vers l’intérieur du tube. La méthode des filaments présente l’avantage d’une préparation rapide et facile par enlèvement d’un seul copeau continu confrontée à la seconde méthode où les opérations d’usinage sont compliquées. L’immersion dans des milieux agressifs comme l’acide sulfurique et le mélange toluène-méthanol a montré les effets de dégradation causés sur ces types d’éprouvettes. Les propriétés mécaniques obtenues avec les filaments sont en général supérieures (entre 6% et 14%), mais dans le cas de H2SO4, l’écart peut atteindre jusqu’à 32% en comparaison avec les éprouvettes témoins. La relation linéaire entre E et σy est préservée dans les milieux agressifs comme dans l’air indiquant l’utilité de tester des filaments en HDPE.

Mots Clés : polyéthylène, tube, propriétés mécaniques, paroi tubulaire, milieu agressif, dégradation.

Abstract:
In this paper, results of two experimental studies are presented and compared. They concern the evolution of mechanical properties through the wall of a HDPE pipe used to transport natural gas. In the first study, specimens filaments (ISO 3341) machined in the form of continuous and uniform chips are used, while the second considers standard shapes according to ISO 527. Both approaches have shown that there is a significant variation in the mechanical properties through the tube wall from the outer side towards the inner side. The filament method is quicker and easier in preparation compared to the second method which comprises complicated machining operations. Immersion in aggressive environments such as sulfuric acid and toluene-methanol showed degradation of major properties. The mechanical properties obtained with the filaments are generally greater (between 6% and 14% higher), but in the case of H2SO4, the difference can reach up to 32% in comparison with control samples. The linear relationship between E and σy is preserved in those oxidative environments indicating the usefulness of HDPE filaments testing.

Keywords: polyethylene, pipe, mechanical properties, pipe wall, aggressive environment, degradation.

1. Introduction
Pressurized plastics pipes have been used successfully for several decades, especially, those made out of polyethylene (PE). In 2007, the worldwide demand for pipes was about 3.7 million tons and a growth rate of
6% per year up to 4.9 million tons is expected in 2012. Based on results from internal pressure tests, the standard extrapolation method described in EN ISO 9080 classifies these pipe grades by their minimum required strength (MRS) to ensure service times of at least 50 years. Nowadays, modern materials with the classification PE 100 (MRS/10 MPa) and above are available [1]. Mechanical properties of HDPE are the subject of several studies concerning various aspects, such as the variation of the physical and mechanical properties in relation to the molecular structure [2], the mechanisms of fracture [3] and the effects of environments during service [4]. During extrusion, the plastic pipe material is subjected to heat and shear forces and also exposed to oxygen, light, heat and water flow during their service life. All these factors cause degradation of the material, resulting in changes in chemical, physical, mechanical and esthetical properties. In order to improve the material’s durability and to protect it against thermo-oxidative degradation, the material is stabilized with different types of antioxidants [4,5]. The strongly oxidizing acids may chemically attack plastics, provoke fading and substantially degrade the mechanical properties. Organic liquids such as fuel oils, mineral oils and organic solvents cause swellings, softening or the dissolution of polymer, the possible degradation of plastics can be due to several physical and chemical phenomena: permeation (solvent ingress, driven by chemical activity gradient), swelling (interaction between the solvent and the polymer matrix), and plasticizer extraction (loss of antioxidants, fillers, heat stabilizers, plasticizer due to the solvent permeation) [5]. In the immersion tests of plastics in liquid chemical products, usually appearance change is a first indicator of physical properties change.

The objective of this study is to present a new approach to investigate the mechanical heterogeneity through the wall thickness of a resistant HDPE pipe using machined filaments and machined standard specimens exposed to chemical environments representing part of the ground aggressiveness.

2. Experimental approach

The material used in this study is extruded by STPM CHIALI Co. (Algeria). The HDPE resin is obtained by addition polymerization, whereas the tubes are obtained by co-extrusion. Typical properties of HDPE-80 and HDPE-100 polymer are provided in Table 1. It should be noted that filament data are obtained using HDPE-100 and HDPE-80 standard (ISO) specimens were respectively machined from pipes having diameters of 200 mm and 125 mm. The machining operations were difficult since the material was not rigid enough to be maintained on a lathe so that special fixtures in the form of chucks were fabricated for each diameter case.

Table 1: Some mechanical properties of HDPE pipe materiel

<table>
<thead>
<tr>
<th></th>
<th>HDPE-80</th>
<th>HDPE-100</th>
</tr>
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<tbody>
<tr>
<td>Density</td>
<td>&gt;930 kg/m³</td>
<td>&gt;930 kg/m³</td>
</tr>
<tr>
<td>MFI</td>
<td>0.2-1.4 g/10 min</td>
<td>0.2-1.4 g/10 min</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>0.55-1 GPa</td>
<td>0.55-1.4 GPa</td>
</tr>
<tr>
<td>Yield strength</td>
<td>≥ 15 MPa</td>
<td>&gt; 19 MPa</td>
</tr>
<tr>
<td>Toughness</td>
<td>2-5 MPa.m¹/²</td>
<td>2-5¹ MPa.m¹/²</td>
</tr>
<tr>
<td>Softening temperature</td>
<td>390 K</td>
<td>390 K</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>≥ 20 min</td>
<td>≥ 20¹ min</td>
</tr>
<tr>
<td>Resistance to cracking in surface-active environment</td>
<td>≤ 15 mm/day</td>
<td>≤ 15¹ mm/day</td>
</tr>
</tbody>
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2.1 Machining conditions:

In order to measure the mechanical properties in every layer within the pipe wall (radial direction); two approaches are used based on machining process. In the first case, regular shaped filaments are prepared across the pipe wall using through wall cutting (figure. 1a), while in the other case, standard (ISO) specimens at different pipe wall locations are extracted (figure. 1b). Therefore, we needed to achieve specimens with the following criteria: (1) the specimens should be directly extracted from the pipe to conserve the intrinsic thermo-mechanical history, (2) they should obey a reproducible preparation methodology, and (3) structural morphology disturbances should be kept to a minimum through the reduction of contact stresses during the automatic machining operation. It is also understood that machining of HDPE material, by chips removal, must take into account manufacturing conditions, material characteristics and applied stresses as well as the interactions between these various criteria especially in terms of heat generation and surface roughness [6].
2.2 Testing conditions

Both filament and standard specimens are subjected to monotonic tensile loads using a Zwick-1120 universal testing machine especially designed for polymer characterization and equipped with a 2 kN load cell. The TestXpert® software controlled the experimental output data and recorded the checked information in real time using an RS232 computer interface. A 1.66 mm/s testing speed was used and the setup was monitored with a computer program that allowed carrying out all tests in exactly the same way on the basis of the general recommendations of ASTM D-638. The selected conditioning environments are combination of various chemical agents which can be present underground or transported with the fluid in contact of the pipe surface. The environments are sulfuric acid (H₂SO₄ at 20%), 50-50 % mixture of toluene–methanol and water. For every testing environment, each batch of prepared specimens was immersed in a tight glass jar for 7 days to ensure that saturation state was obtained [7]. The measured properties are illustrated as a function of the dimensionless thickness (t/t₀) where t₀ is the initial wall thickness and t is the remaining thickness at which the specimen is removed starting from the outer pipe layer.

3. Results and discussion

3.1. Mechanical behavior

Figure 2 illustrates a typical stress-strain curve delivered by the TextXpert software report. Three distinctive zones characterized the behavior: (1) a linear elastic region, (2) a cold-drawing region enclosed between points A and B and (3) an ultimate material tearing coupled with failure. This curve intrinsically identifies the behavior of semi crystalline polymers, which are normally more ductile, especially between the glass transition temperatures, and undergo cold drawing before ultimate failure. Careful observations indicated that cold drawing was initiated just after the yield point and before point A (figure 2). After point B, strain hardening took place, and the stress rose until crystal blocks became aligned parallel to the stretching direction when a fibrillar structure was formed. Figure 2a illustrates the stress-strain behavior of HDPE filaments subjected to the open air for all the specimens that could be prepared from the through machining across the pipe wall [7,8].
The same test is performed on standard specimens representing the totality of the pipe wall for various environments. In all cases, the open air data showed the best properties. Although the shapes of the curves are closer, major differences are obvious in terms of dispersion of mechanical characteristics. For instance, comparing figures 2a and 2b, it is noted that globally stress-strain behavior represents a typical semi-crystalline polymer with specific values for each case.

3.2 Mechanical properties

The most important results are summarized in figure 3. It is clear that all mechanical properties vary across the pipe wall whether considering either specimen shapes. In air, standard modulus of elasticity varies from 600 to 900 MPa, whereas for filaments, it does not exceed 700 MPa.

FIG. 3–Young’s modulus, yield stress and failure strain evolutions in various environments respectively: (a,c,e) for ISO (standard) specimens and (b,d,f) for machined filaments [7,8].
This trend is also noticed for yield stress (obtained at 0.2% strain) with 24 and 9 MPa respectively for standard and filament specimens. In addition, filaments are shown to be more deformable as ε at failure reached 800% compared to merely 600%. For the interaction of filaments with the toluene-methanol solution, it is found that the yield stress is definitely smaller and the threshold stress of matter flow which occurred at slightly more important deformations compared to air results. The drawing phenomenon being located at around 11 MPa is appreciably shortened than that of air. With regard to the onset of plastic hardening, the slope is reduced and the strain at failure reached the 950% limit with less dispersion before rupture. For sulfuric acid, the HDPE presented a behavior contrasting that of toluene-methanol environments. The yield stress is comparable with that of the air case if not slightly lower but the dispersion of the curves is important. It is found that the mean drawing stress is also similar to that of the air (~12.5 MPa) for all considered environments. The zone of plastic hardening remains comparable but the strains at failure approached approximately 1000%, which represents more than 200% compared to the air.

For standard specimens, some properties are completely deteriorated in toluene-methanol mixture compared to the air case [8]. The effect of toluene-methanol mixture is still dominant and these results are confirmed from the literature studying the behavior of polymers vis-à-vis of organic solvents. The decrease in modulus of elasticity (E) after exposure to toluene and methanol is (~ 40%) lower compared with standard specimens exposed to air. Through the pipe thickness, some fluctuations of (E) are pointed out but it seems that the lower values are basically at the outer pipe layers in the following order as a function of environment [7]:

\[ E_{(\text{Sulph Acid})} < E_{(\text{Tol-Meth.})} < E_{(\text{Air})} \]  
(1)

On the other hand, when comparing failure strain which is basically the opposite case for both elasticity modulus and yield stress, it is found:

\[ \varepsilon_{f (\text{Tol-Meth.})} > \varepsilon_{f (\text{Sulph acid})} > \varepsilon_{f (\text{Air})} \]  
(2)

In a recent study, results show that the mechanical properties were relatively degraded during aging time. In fact, tensile modulus and tensile strength of aged samples were reduced. We note that after 6 months of immersion in synthetic sea water at 70 °C, coating samples showed only 14% and 13.5% reduction, respectively in elastic modulus and tensile strength. On the other hand, a more important degradation is observed for water-immersed samples. Indeed, about 33.5% reduction in elastic modulus and 21% in tensile strength was found in such coating samples immersed in water solution. This result reveals the negative effect of hygrothermal aging on mechanical properties. Such result may be explained by the penetration of molecular solvent into the polymer structure, which unconditionally decreases material resistance. It is noted that (E) is drastically affected by organic solvents as shown in figures 3a and 3b for both ISO and filaments specimens. The diminution of (E) is as high as 66% and 35% for filaments and standard specimens respectively. One important result indicates that (E) is increasing through pipe wall from outer towards inner layers. This implies that a structural gradient exists throughout the thickness and is mainly caused by morphological gradients and varying internal stresses. When comparing failure strains, it is observed that obtained values are almost two folds in spreading; i.e. 300-550% and 600-1600% for standard and filaments specimens respectively (figs. 3e and 3f). This difference is probably due to specimen preparation as filaments are deformed much more and solvents may go deeper into the material because of a lesser available specimen volume.
However, in the case of air environment, the obtained values are very similar indicating the opportunity of polyethylene filaments (non-standard specimen geometry) to be used to study mechanical properties throughout the pipe wall as they require less machining and therefore, shorter preparation times compared to ISO specimens. In addition to being a hydrocarbon, HDPE is a non-polar polymer, which makes it vulnerable to attack by solvents such as alcohols, detergents, halogens and aromatics, as well as chemicals such as naphtha and petroleum derivatives [3-5]. Figure 4 describes the relationship between the yield stress and the modulus of elasticity predicting a linear correlation between these two properties for PE and how it correlates also with other data from literature (literature data: HDPE1, $M_s/M_w=1.19$ quenched in ice; HDPE2, $M_s/M_w=2.89$ slowly cooled [7]). This prediction was also checked for HDPE 80 of filaments tested in air. It is therefore interesting to see the validity of this approach in the case of interaction with aggressive media. The results indicate that the linearity is preserved for water, toluene-methanol, and sulfuric acid. The obtained relations for HDPE 80 respectively in T-M solution, $H_2SO_4$ and distilled water are:

$$\sigma_{yy}_{HDPE80,M=Mo} = 0.0104 E_{HDPE80,M=Mo} + 14.625 \quad (R^2 = 0.961)$$ (3)

$$\sigma_{yy}_{HDPE40,H2SO4} = 0.0081 E_{HDPE40,H2SO4} + 17.050 \quad (R^2 = 0.665)$$ (4)

$$\sigma_{yy}_{HDPE80,water} = 0.0113 E_{HDPE80,water} + 15.283 \quad (R^2 = 0.738)$$ (5)

4. Conclusion
This study allowed drawing some relevant conclusions:

1. Both methods are convenient to study material mechanical heterogeneity and associated environment effects for HDPE pipes.
2. Stress-strain curves are similar in shape but comprise different characteristic values which imply that comparison can be done.
3. Mechanical properties are found to be evolving throughout the pipe wall.
4. Higher properties (stresses and modulus) are noticed at the pipe bore while higher deformation properties are dominant the outer pipe surface (strains).
5. Toluene-methanol solutions are found to be very effective in degrading stress components while sulfuric acid basically affects strain ones.
6. The linear correlation between the $\sigma_y$ and $E$ is preserved as well as in air and in studied environments.

Acknowledgements:
The authors would like to thank STPM-CHIALI Co. (Algeria) for sample donation and Pr N. Aouf of LCOA (UBM Annaba) for supplying chemical solutions. This work is part of the PNR Project 11/U23/1177 (2012).

References