Degradation of plastic pipe surfaces in contact with an aggressive acidic environment

Wafia Ghabechea,b*, Latifa Alimi a,b, Kamel Chaoui a

Abstract

Polyethylene (PE) pipes transporting water are vulnerable to aggressive agents which are able to diffuse through buried plastic pipes causing oxidative degradation. The latter may occur as a result of a spontaneous chemical reaction with atmospheric oxygen or as an induced oxidizing reaction with disinfectant agents (i.e. chlorine or hypochlorous acid ions) which are commonly added to municipal water supplies for public health reasons. Basically, PE pipes surfaces undergo undesired oxidation reactions whenever they are in contact with adverse external environments and/or when conveying fluids which tend to modify internal pipe wall structure. In this work, the effects of distilled water and diluted hydrochloric acid at different concentrations on the external and internal surfaces of a high density polyethylene (HDPE-100) pipe are studied. The measured parameters are roughness and hardness in order to appreciate surface quality variances in as-received and degraded materials. Initially the outer surface is rougher than the inner’s one but in contact with distilled water, the external surface roughness increased by 6% although the internal face of the tube revealed a small decrease (<5%). When exposed to hydrochloric acid, pipe roughness (μm) showed a substantial increase as a function of increasing medium concentration. Crystallinity (χ in %) measurements confirmed the gap between outer (51.55%) and inner (61.31%) surfaces indicating that degradation has taken place at the structural level when HDPE was in contact with such aggressive agents. On the other hand, it is revealed that after exposure to oxidizing environments, crystallinity dropped by approximately one third when compared to as-received material; therefore reducing resistance to fracture and subsequently pipe lifetime.

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Keywords: polyethylene pipe; environment; distilled water; diluted hydrochloric acid; degradation; surface roughness; hardness; crystallinity.
1. Introduction

Polyethylene (PE) pipes are widely used by utility companies for transporting potable water, natural gas and for sewage networks. Since such piping networks are installed underground, they usually undergo property changes because of environmental effects (soil aggressiveness, humidity, temperature changes and bacterial attacks). In addition, some physical degradation might be caused during handling and installation operations. To minimize such effects, for the case of seawater intakes and/or marine outfalls, a specially designed production facility is used to extrudate long length plastic polyethylene pipes to be used in the conditions of deep sea [1]. Slurry erosion tests were also performed on several PE pipes at laboratory conditions. It was shown that PE proved to have excellent anti-erosion properties and a correlation between erosion rate (mg/kg) and both fracture energy (J/m^3) and Young’s modulus (MPa) is elucidated. This study presented also the impact effects of solid particles contained in the mud drains on the plastic surface [2]. In another study, polyethylene used as coatings for steel pipe was subjected to fluid-borne sand particle under erosion conditions. It was deduced that PE erosion resistance followed a power law dependency on particle kinetic energy and the medium density PE showed the best surface resistance compared to both flexible and hard polyurethanes, epoxy filled with amines and epoxy packed with SiC fibers [3].

Water industry is using at high rates PE pipes to replace older steel and cast iron mains. Renovation techniques of water mains based on PE pipe linings is also an efficient and economic alternative. However, studies of roughness behavior and mechanical properties changes due to friction and environmental effects should be taken into account as suggested in several studies [3-5].

In a previous study, it was observed that strongly oxidizing acids attack PE provoking major changes in mechanical properties throughout pipe wall [6]. In addition, it was concluded that PE pipes stress components are reduced when exposed to crude oil or toluene-methanol environments whereas strain components are strongly altered in contact with sulfuric acid [6]. Crystallinity distribution across the pipe wall, a consequence of the manufacturing process, was cited as the cause of such changes. These results were also confirmed in a recent study involving HDPE-80 pipe resins oxidation under chemical short-term conditions [7]. Most of these studies did not discuss the extent of changes between outer and inner pipe surfaces although it is advanced that the revealed morphology from the outer skin was spherulitic, and that the spherulites had a mostly banded appearance. Subsequently, it was not possible to distinguish an oriented skin layer at the surface of the pipe either by atomic force microscopy (AFM) or polarizing microscopy [8].

The objective of the present study is to compare outer and inner PE pipe layers using measured surface properties (roughness and hardness) and to establish the differences in crystallinity. Subsequently, the effects of distilled water and a strong oxidizing environment i.e. hydrochloric acid are presented.

2. Experimental approach

2.1 Specimen preparation

HDPE-100 polyethylene pipe, used in this study, is kindly supplied by National Electric & Gas Co. (SONELGAZ, Annaba, Algeria). The pipe is manufactured by CHIALI Company (Sidi Bel-Abbes, Algeria). Some properties of the as-received material are summarized in Table 1.

For this study, all prepared samples were checked to be free from any surface alteration. It has been observed that some surface alterations existed basically due to mishandling and unwanted contacts with other objects during storage or transportation as shown in Figures 1a and 1b. The outside pipe diameter and the wall thickness are respectively 113 mm and 11 mm. Standard tensile testing specimens were cut from each pipe surface according to the general recommendations of the standards ISO 527 and ASTM D-638 (Fig. 1c). Environmental Stress Cracking (ESC) test specimens were carefully prepared using a lathe followed by a small milling machine at very low speeds. Each prepared ring is used to produce a maximum of 5 arched specimens. Each specimen is 20 mm high and has a curved length of 20 mm (Fig. 1d). Each testing condition should contain not less than 5 valid specimens. During roughness or hardness measurements, any deviating value should be repeated elsewhere in the same specimen and
can be disregarded in case of detected surface defect.

Table 1. Material properties (according to manufacturer)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>≥ 930 kg/m³</td>
</tr>
<tr>
<td>Melt Flow Index (MFI)</td>
<td>0.2-1.4 g/10 min</td>
</tr>
<tr>
<td>% black carbon</td>
<td>2-2.5 %</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>0.55 - 1 GPa</td>
</tr>
<tr>
<td>Yield Stress</td>
<td>20-30 MPa</td>
</tr>
<tr>
<td>Strain at failure</td>
<td>≥ 350%</td>
</tr>
<tr>
<td>Shore Hardness (HS)</td>
<td>61-67</td>
</tr>
<tr>
<td>Toughness (KIC)</td>
<td>2-5 MPa.m½</td>
</tr>
<tr>
<td>Oxidation Induction Time (OIT)</td>
<td>≥ 20 min</td>
</tr>
<tr>
<td>Environmental Stress Cracking Resistance (ESCR)</td>
<td>≤ 15 mm/day</td>
</tr>
</tbody>
</table>

Fig. 1. (a) Typical defects encountered during storage of pipes HDPE outer skin, (b) Distinctive scratch, (c) Shape and locations of specimens taken from pipe surfaces for standard tensile tests, (d) Specimens for ESC tests (2 x 2 cm²).

As-received specimens are conditioned in dry tight plastic containers until measuring date. ESC specimens are immersed in respective environments for determined periods and isolated from ambient air using tight covers. The environments considered in this study are: (i) distilled water (as a wet reference), (ii) hydrochloric acid (HCl) at 3 different concentrations (1%, 10% and 20%) in order to examine the acidic diluted conditions.

The data presented in this study is relative to an exposure time of 43 months. Prior to each measurement, the sample is rinsed with distilled water, allowed to dry freely in open air and identified accordingly. Specimens and containers are stored at laboratory temperature.

2.2 Characterization techniques

Roughness is followed on the outer and inner faces of each sample (eq. 1). The roughness criteria measured is the average height of profile or the sum of the highest heights and deepest lows (Rz) as defined by DIN-4768 (1990).
\[
R_Z = \frac{1}{n} \left( R_{Z1} + R_{Z2} + \ldots + R_{Zn} \right)
\]  

(1)

The value is automatically measured with a Surftest-201 type (SJ-201M) Mitutoyo roughness meter consisting of a diamond stylus with a mechanism for automatic removal and storage of measured data. The diameter of the tip is 5 microns and moves linearly over a length of 4 mm analysis with a width of 0.8 mm. It has a measuring range up to 350 μm (-200 μm to 150 μm) and can have a surface texture using different roughness parameters. These conditions are well adapted to measurements of the roughness of HDPE pipes. The following equation is used to calculate roughness criteria:

\[
R_Z = \frac{1}{5} \sum_{i=1}^{5} Y_{pi} + \frac{1}{5} \sum_{i=1}^{5} Y_{vi}
\]  

(2)

With: \(Y_i\): deviations from a mean line, \(Y_{pi}\): highest profile peak and \(Y_{vi}\): depth of the lowest profile.

Roughness measurements were carefully made on each of the dry specimens. Each value is the average of 6 measurements at different locations and the estimated uncertainty is approximately 0.01 μm.

On the other hand, Shore hardness (HS) measurements were performed using a Mitutoyo durometer Hardmatic (HH-401) based on a statistical protocol for both specimen surfaces. This test is normally the rebound of a spherical calibrated carbide projectile at a determined rate on the material to be tested; the harder the material the higher the rebound. When the projectile strikes the surface, the loss of kinetic energy that results from surface deformation is calculated using velocity measurements. The device measures the ratio of rebound speed compared to the impact speed. The Leeb hardness value, \(HL\), is calculated from the ratio of the impact and rebound speed according to equation 3:

\[
HL = \frac{V_R}{V_I} \times 1000
\]  

(3)

With: \(V_R\): rebound velocity, \(V_I\): Impact velocity

Hardness reading is electronically displayed on a screen after recording corresponding signal voltages owing to projectile movements. It should be noted that because of specimen curvature, inner surface hardness measurements should be carefully carried out by ensuring the true complete contact of the probe with a flat plane.

Mechanical testing was performed on standard tensile specimens (Fig. 1c) by means of a Zwick 1120 test machine with a load cell of 2 kN at 100 mm/min equipped with a Zwick extensometer. Testing was controlled by the computer program TestXpert, Ver. 9.01. The observation of the two surfaces morphology was carried out by using Scanning Electron Microscopy (SEM) and the metallization is performed by depositing a layer of gold. Crystallinity was measured using an X’pertPro (PANalytical) X-ray diffractometer. A scan rate of 2°/min at 2000 cycles using CuKα radiation of wavelength 1.596 Å was applied. A radial scan of Bragg angle versus intensity was obtained with an accuracy of ± 0.25° at the location of the peak. The processing of diffraction patterns was checked with the standard XRD one (JCPDS card No. 11-834). Crystallinity (\(X_c\)) is determined using equation (4):
with: $I_{cr}$, $I_{am}$: scattering intensity of crystalline and amorphous structures respectively.

Samples of (15 ± 2) mg, taken from the two surfaces of the sample, were analyzed by drawing a tangent to the steepest portion of the exothermal curve using a 200-PC-NETZSCH differential scanning calorimeter (DSC) to determine the oxidation induction time (OIT) in agreement with EN 728 AFNOR at 200°C in an oxygen flow of 50 mL min$^{-1}$ ± 10%. The deviation from the baseline when oxidation starts was used as a criterion for induction time, which was obtained by extrapolation.

3. Results and Discussion

3.1 Tensile tests

True stress-strain behavior of outer and inner machined standard specimens is presented in figure 2. The dispersion at each side is rather small and remains negligible although the global shape is very similar and representing a typical semi-crystalline polymer. It is noted that inner surface presents better mechanical properties and such findings are confirmed in other studies [6, 7, 9, 10]. Table 2 gives more detailed comparison for different pipe layers.
The plastic hardening is important at the outer surface most probably because of higher compressive residual stresses imparted by extrusion. In Shouwenaars et al. study [9] which uses compact tension specimens, it was found that ultimate tensile strength (UTS) and Young’s modulus (E) on the inner side were higher by 12.6% and 18.7% respectively compared to the outer surface (Table 2), while in Alimi et al. works [10], based on ASTM Type IV specimens, similar observation were made. In a related study exploiting machined filament from HDPE pipe, it was shown that there is an evolution of mechanical properties across pipe wall [6]. After immersion in medium, the mechanical properties fall considerably, for example, in table 2 in filament case [6], we can perceive the effect of HCl who degrade \( \sigma_{\text{max}} \) and E by 30% and 57 % respectively for inner surface, for outer surface \( \sigma_{\text{max}} \) and E drop by 45 % and 75 % respectively. We can observe that the effect of HCl on outer surface was more pronounced that on inner surface.

<table>
<thead>
<tr>
<th>Surface (Layer)</th>
<th>( \sigma_{\text{max}} ) (MPa) Before immersion</th>
<th>( \sigma_{\text{max}} ) (MPa) After immersion (7 days) As-received materials</th>
<th>E (MPa) Before immersion</th>
<th>E (MPa) After immersion (7 days) As-received materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After immersion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distilled water</td>
<td>24.1(a)</td>
<td>20.58(d)</td>
<td>455(a)</td>
<td>575.95(d)</td>
</tr>
<tr>
<td>HCl</td>
<td>28±0.5(b)</td>
<td>10.04(e)</td>
<td>287.5±43.75(b)</td>
<td>259.80(e)</td>
</tr>
<tr>
<td>Middle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials</td>
<td>22.5(a)</td>
<td></td>
<td>400(a)</td>
<td></td>
</tr>
<tr>
<td>After immersion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distilled water</td>
<td>15.7(c)</td>
<td></td>
<td>780(c)</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials</td>
<td>21.6(a)</td>
<td>20.98(d)</td>
<td>370(a)</td>
<td>333.82(d)</td>
</tr>
<tr>
<td>After immersion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distilled water</td>
<td>24.75±0.375(b)</td>
<td>8.06(e)</td>
<td>188.3±19.16(b)</td>
<td>156.13(e)</td>
</tr>
<tr>
<td>HCl</td>
<td>14.8(c)</td>
<td></td>
<td>640(c)</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) [9], 18 mm, CTS (Constant Tensile Stress)
\( b \) Present work, 11 mm, ASTM D-638, Type IV
\( c \) [6] 11 mm, filament specimen
\( d \) [7] 11 mm, ASTM D-638, Type IV

3.2 Roughness

In the SEM micrographs of the unexposed samples (Fig. 3: As-received), inner and outer surfaces appear smooth, with different morphologies that result from the extrusion processing conditions. It is observed that inner surface presents a small and mostly asymmetric spherolitic texture as confirmed in Trifonova et al. study; however, for the outer surface, such texture does not appears, as a result of the extrusion process cooling conditions [8]. In case of distilled water, the inner surface texture looks similar to the as-received samples with a little change in colour which is a sign of oxidation reactions. For samples exposed for long periods of time in HCl 20% (43 months), a degradation of outer surface is more pronounced, which is in agreement with roughness measurements. We suggest that alteration of surface may be due to antioxidant (AO) migration. In figure 3, we can observe similar agglomerates of AO and other additives like black carbon especially for outer surface for both distilled water and HCl 20% cases.

Concerning roughness measurements, the as-received pipe showed higher values at the outer surface, the difference between the inner and outer surface is almost double (Fig. 4: As-received). Again, processing conditions are responsible for these discrepancies most probably caused by a state of compressive internal stresses resulting from water cooling of the outer pipe layers [6].

After immersion in distilled water, roughness for inner surface decreased by 4.9% while for the outer surface, it increased by 6.2% (Fig. 4: Distilled water). The two folds difference that existed before exposure to distilled water is roughly maintained after contact. Polyethylene material surface is usually hydrophobic and therefore resists to water while under wet conditions and in the presence of pollutants, a gradual loss of hydrophobicity occurs. The
swelling phenomenon of PE has been identified and can be worsened by other parameters such as external pressure or antioxidants migration.

![Swelling phenomenon of PE](image)

Fig. 3. Scanning electron micrographs of a) internal and b) external upper surface of the pipe

In this study, it was interesting to study the effect of a strong acid such as HCl in order to highlight the behaviour of HDPE pipe in contact with chloride ions. Indeed, several studies have been conducted to verify the role of chlorine in H2O on the degradation of the tubes used for drinkable water. It has been shown that chlorine and its derivatives deteriorate the properties of the HDPE especially by combining heat [9]. For the inner surface (Fig. 4: Inner surface), it was found that the roughness increases in contact of HCl. This effect is proportional to the concentration when the latter was varied from 1% to 10% and 20%. This observation is similar to the outer surface results but with larger values (Fig. 4: Outer surface). This can be explained by two factors: First, it is observed that surface roughness values at the initial state indicate that $R_z$ (outer surface) is less than $R_z$ (inner surface), which means that, for [HCl] = 1%, the start is made from two different values who are $R_{z\text{, internal}} = 2.63 \mu m$ and $R_{z\text{, external}} = 4.67 \mu m$. Second, it is known from literature that these two surfaces have different structures in terms of internal stresses and crystallinity [9]. By varying the concentration, it was observed that the effect of HCl on two surfaces is not very pronounced up to 20% (Fig. 4). We suggest that physical loss of antioxidant in aggressive medium, can affect surface texture (section 3.4).
Compared to distilled water, it is concluded that HCl effect is more significant and with the probability of engendering more damage to pipe integrity. For both surfaces, a second order polynomial function is used to describe the obtained data:

\[ R_{z_{\text{inner surface}}} = 1.19 \, C + 2.7 \quad (\text{Corr. } R^2 = 0.88) \]  
(5)

\[ R_{z_{\text{outer surface}}} = 0.33 \, C + 5.17 \quad (\text{Corr. } R^2 = 0.98) \]  
(6)

With \( C \): hydrochloric concentration, \( R \): correlation factor.

3.3 Hardness

Hardness measurements for the as-received pipe showed higher values at the outer surface. The difference (~19.3%) is almost 25% higher than inner surface (Fig. 5: As-received)
For distilled water, hardness analysis showed a clear decrease after water contact indicating a sort of material softening and the changes are 18% and 14% for outer and inner surfaces respectively (Fig. 5). It is suggested that the process of crystallization has a direct influence on hardness of thick products as it occurs inside the solidifying material (from the melt) at elevated temperature. Usually, such conditions are unfavourable for strength and toughness of polymers [11]. The outer surface is probably more willing to absorb water; this should have a relationship with the nature of the morphology of extruded HDPE.

The hardness values in HCl are smaller than those measured in the case of distilled water and regardless of the concentration of HCl. The percentages of reduction of the hardness of HDPE under the effect of 1% HCl are 32% and 41% respectively for the inner and outer surfaces.

3.4 Crystallinity

The WAXD analysis carried out on both surfaces showed 2 peaks at 21.5 and 23.9 which are characteristics of (110) and (200) lattice planes respectively (Fig. 6). The main observation in the present work, for as-received materials, indicated a modest change in peaks’ position throughout the scan range and no significant changes of the inter-planar distances ($d_{inner}$=0.408 nm; $d_{outer}$=0.415 nm). Crystallinity measurements indicated a difference of 15.9 % in favor of inner surface layers; this is one worthy and plausible explanation for the better mechanical properties at this pipe side (Fig. 6).
For the previously discussed environments (Fig. 7), two basic results are deduced: (i) inner side crystallinity is always higher compared to outer surface and (ii) exposure to DW and HCl reduced crystallinity up to 30% especially for hydrochloric acid. The measured crystallinity values are shown in figure 6 for all cases. These findings are confirmed from literature review which indicates that usually $X_C$ is evolving across the pipe wall from the outer to the inner surface [12, 13]. Similar trend is also confirmed even when PE is exposed to aggressive environments which can lead to cracking [14]. To explain the decrease of crystallinity we suggest that just on upper surface (skin), there is no post-crystallization process; it might be possible that the inner pipe was crosslinked during the manufacturing process and prevented the re-crystallization to occur. Terselius et al. suggested that a crosslinked structure is unable to allow large chain rearrangement, which ultimately prevents the polymer chain to re-align [15].
3.4 Oxidation induction time (OIT)

Lifetime obviously depends on the additive package used. The consumption of stabilizers leads to enhanced degradation, thus principally the measurement of stability (OIT or degradation temperature) should be related to the expected service life. OIT represents the time necessary for a significant depletion of stabilizers and built-up of a sufficient quantity of hydroperoxides, which subsequently decompose at an accelerating rate. Mechanical stresses imposed upon plastics exposed to chemically aggressive environment as well as various types of impurities in the environment surrounding pipes may reduce OIT and accelerate the rate of oxidative degradation [16,17].

Initially, OIT of outer surface is higher than the inner one (~ 14 % of difference). Right after the extrusion process, outer surface is quenched with water baths that fixes antioxidants in outer layers of pipe (metallic agglomerate, with ~5μm of diameter, become visible in Fig. 3), while the antioxidants are consumed by atmospheric oxygen surrounding inner surface, during slow cooling at open air, (Fig. 8). In distilled water, OIT decrease for the two surfaces and the difference was maintained in favour of outer surface. For hydrochloric acid, we suggest that antioxidants are consumed by two different methods for the two surfaces. In inner surface, by extraction: antioxidants will diffuse to the surface of the pipe; because of amorphous structure how offer large space for the antioxidant to pass into solution (physical consumption). In outer surface by chemical consumption, antioxidants react chemically with an oxidizing species to protect the polymer. This reaction can occur on the surface, or aggressive species can diffuse to the interior of the polymer, and take place in the core of the polymer. It’s found that consumption by the chemical reaction is negligible against physical loss by extraction [18].
In hydrochloric acid, the behaviour of two surfaces changes, antioxidants consumption becomes more important in outer surface especially for the [HCl] = 20%, while the inner surface presents better resistance, which agrees well with the SEM observations and the explanation of Yu et al. [16]. The decrease of OIT for the two surfaces in HCl, obeys to linear law (eq. 7 and 8) and the loss of antioxidants is faster than outer one’s.

\[
OIT_{\text{inner surface}} = -1.85C + 25.5 \quad (\text{Corr. } R^2 = 0.729) \tag{7}
\]

\[
OIT_{\text{outer surface}} = -10.57C + 32.91 \quad (\text{Corr. } R^2 = 0.987) \tag{8}
\]

With C: hydrochloric concentration.

4. Conclusions

The phenomenon of rupture due to stresses and aggressive environment (ESC: Environmental Stress Cracking) is one of the main causes of HDPE pipes damages. Several factors influence formation and slow crack growth throughout pipes wall. In addition, the nature of the chemical agent and its concentration in soil can largely influence cracking. It is understood that the intensity of service constraint, temperature, exposure time and the quality of the tube surface (roughness) represent other parameters that should be taken into account. The following conclusions may be drawn from this study:

1. Outer and inner surfaces have different mechanical properties, thus implying different textures. It is found that outer surface is rougher than inner one.
2. Immersion for long period in the aggressive environments increases roughness implying a surface degradation which may lead to soil contamination and product loss.
3. The increase of roughness is caused by antioxidants depletion, which degrades the surface texture and lowers mechanical properties.
4. Concerning the contact of the hydrochloric acid with HDPE material, it is proposed that antioxidant loss is a rapid action in nature on the outer surface while it appears slower at the inner surface. The reason is imputed to the pipe wall structure as it is influenced by the extrusion course. This confirms that the
physical oxidation degradation mechanism is dominating at the outer surface while the chemical oxidation is prevailing at the inner pipe face.

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