

FTIR study of HDPE structural changes, moisture absorption and mechanical properties variation when exposed to sulphuric acid aging in various temperatures

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Abstract:

The aging of high density polyethylene (HDPE) when exposed to sulphuric acid solution at room temperature (25°C), 40°C or 60°C was studied. Sorption kinetics was studied through water absorption rate response at different temperatures. Similarly, the diffusion coefficients of solvent molecules and the maximum of the absorbed humidity in the HDPE samples were determined. The activation energy and the mixing enthalpy were also deduced. The structural modifications and chemical changes by the application of Fourier–transform infrared spectrophotometry (FTIR), mainly polymeric chain breaking and branching have been studied. The tensile test results showed that with increasing the aging temperature, the elongation and stress at break of HDPE decreased.

Keywords: high-density polyethylene, accelerated test, hydrothermal aging, degradation, diffusion, chemical changes

1 Introduction

The service life of plastic pipes and the factors influencing it have been the subject of considerable interest for some time. Pipes are used in the most diverse application areas including water, waste water and sewer pipes [1]. These pipes are primarily used for corrosion resistance. Recently, the material based on polyethylene becomes more and more dominant in pipe industry. In fact, it represents a durable, high performance and economical. However, their use in a variety of aggressive environments such as marine, sulphate environments, humidity, wide range of temperature, UV exposure, etc. ..., can affect their lifetime provoking the deterioration of their physical and mechanical properties [2].

Study of natural aging is time consuming; it is necessary to have recourse to accelerated aging, in order to predict the behavior of HDPE at various maturities and with a relatively short time. The accelerated aging is used to control the similarities in behavior compared to natural aging and to allow extrapolations reasoned.

Guermazi et al. [3] have studied the effect of time and aging temperature on structural and mechanical properties of pipeline coating using saline solution, They have found that the elevated temperature induces a drastic mechanical degradation of the polyethylene coating.

Pegoretti and Migliaresi [4] have investigated the long-term effects of aging in water at two testing temperatures on physical and mechanical properties of a composite dental prosthetic material. In particular, they have found that the flexural strength strongly decreased during the hygrothermal aging, moreover, such decrease was accelerated by increasing temperature.

The main objective is to present durability evaluations of such HDPE pipe under sulfate environment. For this reason, solvent absorption was measured as a function of immersion time for different temperatures. The FTIR characterization was also evaluated. A 92 days immersion time, the mechanical properties of the aged samples were evaluated by tensile testing.

2 Experimental part

2.1 Sample preparation

The standard tensile specimen is derived from the inner wall of a double wall corrugated pipes HDPE (FIG. 1a) [NF EN 13476] which is characterized by a diameter of Ø1000mm. This sample was cut in the transversal tube (FIG. 1b).

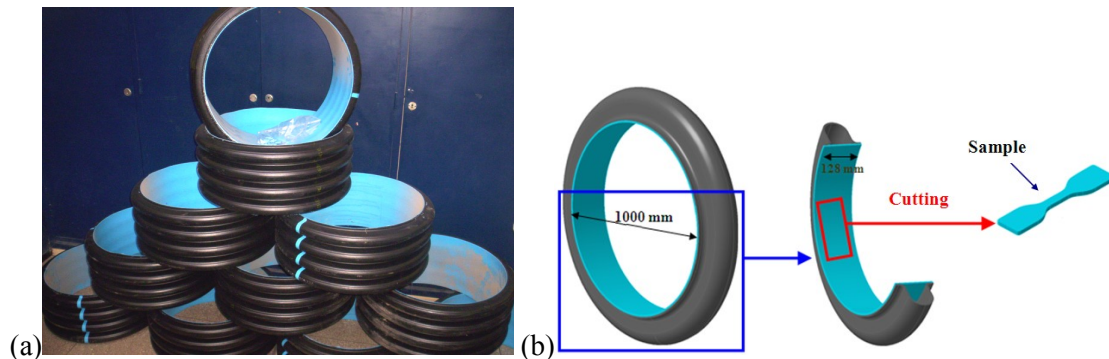


FIG. 1 – Double wall corrugated pipes HDPE standard (a), schematic of the cutting of HDPE samples (b)

2.2 Experimental conditions

A hygrothermal aging procedure that simulates different weathering conditions was adopted. Immersion of HDPE samples was performed for periods going until some days in tubs containing sulphate solution at several temperatures. Three values of temperature were used: room temperature (25°C), 40 and 60°C. This sulphate solution was prepared with 0.5% of H₂SO₄ and having pH 1±0.2.

During the test, samples are taken to observe the evolution of weight gain. At each maturity time the samples are removed from the tray and placed in another pan with water for an hour to rinse.

3 Results and discussion

3.1 Mass gain ratio of HDPE samples in the various temperatures aging over immersion time

As mentioned below, before their isothermal immersion in solution, the studied samples were initially weighted (W_0). Their weight W_t was then determined at various exposure times t and the relative weight gain or the mass gain ratio, $M(t)$, was calculated as follows:

$$M(t) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

Therefore, $M(t)$ is plotted versus the immersion time \sqrt{t} .

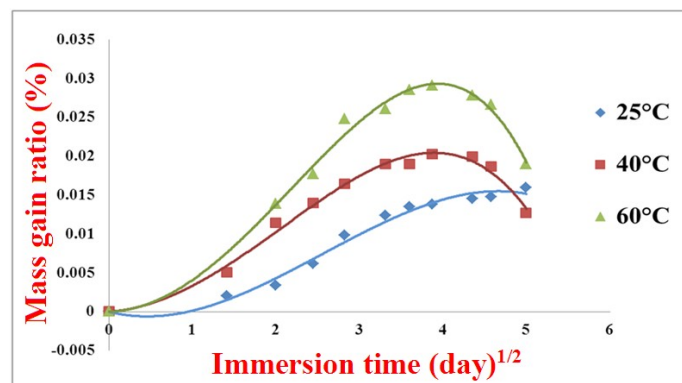


FIG. 2 – Evolution of the mass gain rate versus aging time for HDPE immersed at 25, 40 and 60°C.

As follows, the water absorption rate as a function of the immersion time aging, for HDPE immersed at 25°C, 40°C and 60°C, is shown in FIG. 2.

As plotted in FIG. 2, all the curves reveal that water absorption is a Fickian process characterized by a constant coefficient of diffusion, D , and an equilibrium saturation concentration M_s . Then, the weight gain significantly decreases. These stages can be detailed as follows:

In first approximation, there is a diffusion process of solvent molecules into polymer samples which is characterized by a fast increase in the sample weight with time. Therefore, an equilibrium stage was undertaken after a limited period. Finally, there is a remarkable weight loss process which was superimposed to water sorption.

Moreover, varying temperature has shown that this parameter enormously influences the water sorption response of the studied material. Increasing the aging temperature affects the initial increase of the sample weight, the equilibrium stage and the weight loss process. In fact, FIG. 2 shows that an increase in the temperature leads to acceleration of the diffusion process, reduction in the duration of the equilibrium stage and rise in the equilibrium uptake.

The linearity of the initial stage in the weight gain against $t^{1/2}$ curves was used to determine the diffusion coefficients [3]:

$$D = \frac{\pi}{16} \times \left(\frac{e}{M_s} \right)^2 \times \left[\frac{M(t)}{\sqrt{t}} \right]^2 \quad (2)$$

TAB. 1 summarizes the calculated diffusion coefficients and the saturation concentrations.

Temperature	25°C	40°C	60°C
(Diffusion coefficient D ($m^2 s^{-1}$))	8.8×10^{-13}	1.86×10^{-12}	4.6×10^{-12}
(Equilibrium stage (days))	22	16	14
Equilibrium uptake M_s	0.016	0.021	0.03

TAB. 1 – Diffusion coefficients and equilibrium uptake M_s of water molecules in the HDPE samples.

On the other hand, the last stage which corresponds to the decrease of the mass gain ratio or decrease of the sample weight may be ascribed to many phenomena such as the reorganization of polymer chains, the washing phenomena and the migration of cross-linking agents to the surface during aging process [3,6] or the extraction of low molecular weight compounds, e.g. free monomer [7]. These results are in good accordance with those found in the literature [3,6–8].

Assuming that the coefficient of diffusion of water into HDPE may be considered to be Arrhenius type process, this can be written a:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (3)$$

Where D_0 is a constant, E_D , an activation energy and RT the product of the gas constant ($R=8.32 \cdot 10^{-3}$ KJ/mol) and absolute temperature.

In the same way, the equilibrium uptake, M_s , may be modelled as follows [7]:

$$M_s = M_{s,0} \exp\left(\frac{-\Delta H_s}{RT}\right) \quad (4)$$

Where $M_{s,0}$ is a constant and ΔH_s is the mixing enthalpy.

As follows, both the variations of $\ln D$ and $\ln M_s$ as functions of the temperature, in terms of T^{-1} , are shown in FIG.3.

As it can be seen in FIG. 3, the regression analysis of $\ln(D)$ and $\ln(M_s)$ versus $1/T$ for the three temperatures gives good correlation coefficients and leads to the values of $E_D=39.1$ KJ/mole and $\Delta H_s=14.9$ KJ/mole. These findings correlate with similar results found by other authors [3,7]. Indeed, the first authors

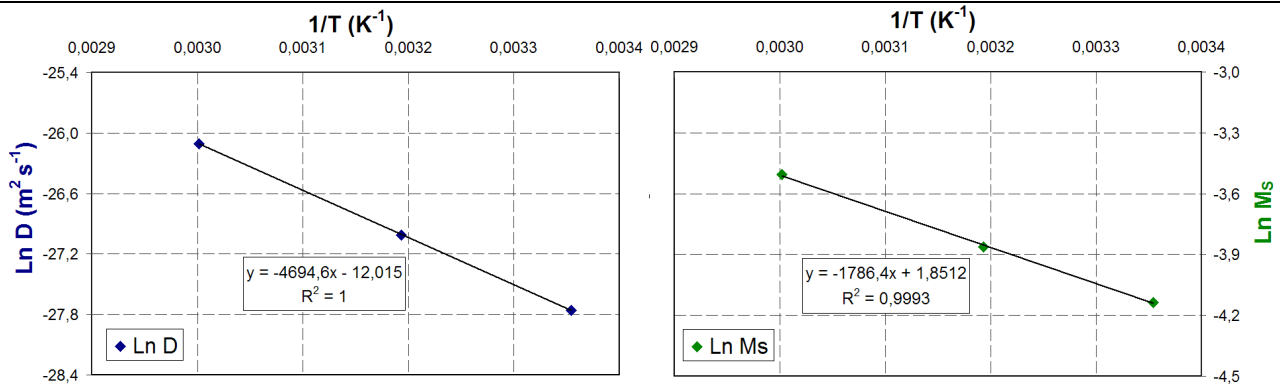


FIG. 3 – Arrhenius plots for the diffusion coefficient (D) and the solubility coefficient (M_s).

[3] have found the same range of values 49.7 and 19.5 KJ/mole for E_D and ΔH_s , respectively, when studying the aging of polyethylene in saline solution (30g/L of NaCl). However, the others [7] have shown the same range of values 55.1 and 4.5 KJ/mole for E_D and ΔH_s , respectively, when studying the aging of polyamide in acid solutions.

3.2 Structural properties

In order to better explain the mechanical degradation observed in [Para 3.3], a structural characterization of the aged material has been investigated through FT-IR analysis with absorbance mode. As follows, the spectra of both aged and unaged samples are shown in FIG. 4. The example of the aged sample was that immersed at various temperatures (25°C, 40°C and 60°C) FIG.4. It seems that its infrared spectra allow us to show clearly if there is really a structural modification induced by aging process.

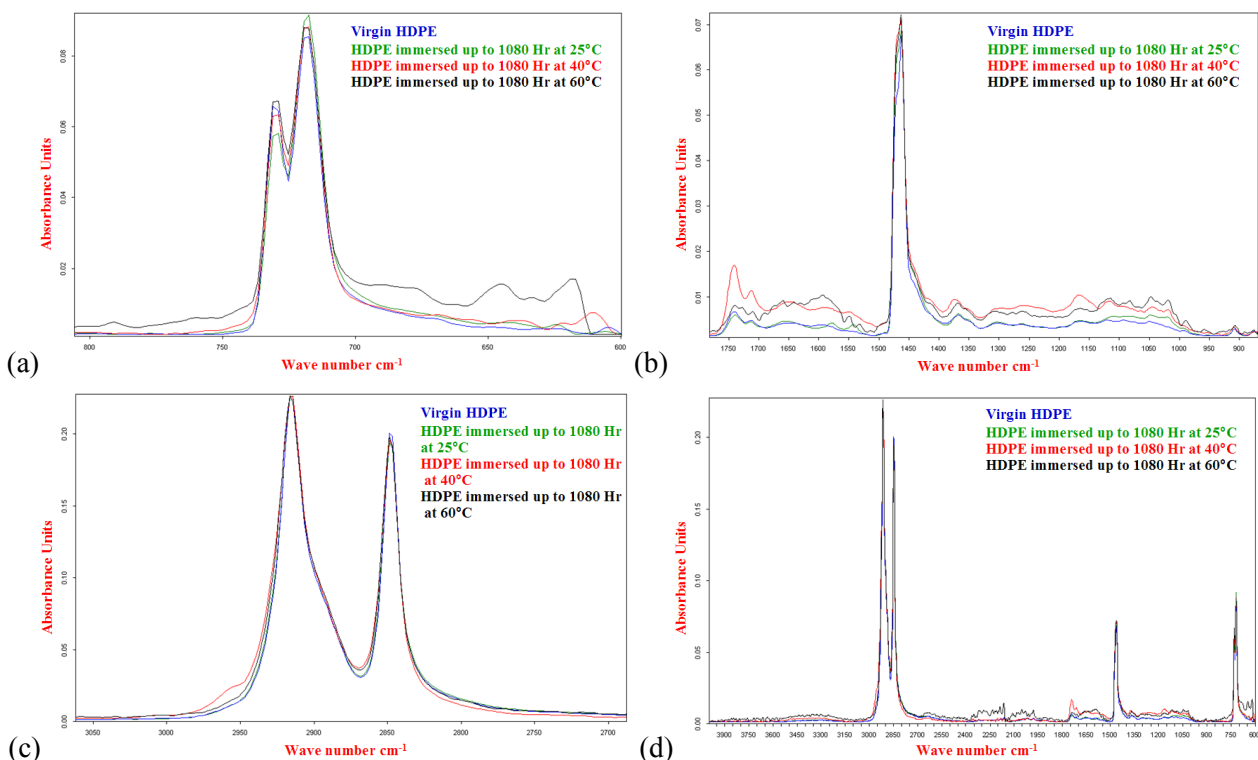


FIG. 4 – HDPE spectra acquired by absorbance mode: unaged sample and aged ones at 25, 40 and 60°C during 1080 Hr. FTIR spectra [600–800] (a), [900–1750] (b), [2700–3050] (c) and [600–4000 cm⁻¹] (d).

FIG. 4 shows the results attained for the spectres of the different samples exposed during 1080 hours at different temperatures and the spectre of the virgin HDPE sample. This figure clearly indicate the influence of temperature immersion well be commented later. Table 2 shows the most significant bands studied, their functional group and the relevant absorption type. Table 3 defines the behaviour of each of the specified bands at different aging temperatures. The type of evolution followed by individual bands indicates whether they grow, decay or remain unaltered. The evolution of the different structural modifications and chemical changes as a function of aging temperature, as deduced from the infrared bands examined, can be seen in

Table 4. From the results obtained, it is worth noting that after 1080 hours of immersion, structural modifications occurs as indicated by the appearance of groups (719, 3400 cm^{-1}), with the appearance of branching (1172 cm^{-1}) and with the formation by oxidation of ketone and ester groups (1368, 1738 cm^{-1} , respectively) and the disappearance of groups (730 and 2848 cm^{-1}). This reflects the beginning of the polymeric chain scission.

The main bands of the studied HDPE consist of a band situated about 2900 cm^{-1} assignable to CH_2 as an asymmetric stretching, a band around 1462–1472 cm^{-1} revealing a bending deformation, and another band at 719–730 cm^{-1} which indicates a rocking deformation [3,14]. Also it was possible to distinguish an asymmetric band, centred at 1600 cm^{-1} , in the spectra (of 40 and 60°C). This corresponds to the bending modes of absorbed water. In the same way, the OH^- stretching band at 3400 cm^{-1} is attributed to water molecules. The same results were previously reported in the works of Guermazi and Gugumus [3,17,18].

The major difference between the spectra corresponding to the unaged and aged sample is only their intensity of bands. A decrease in the intensity signal and the disappearance of certain groups are observed for the aged sample. For example, all the following absorptions (corresponding to 2848, 730 cm^{-1} , etc...) were decreased in terms of intensity. This indicates the beginning of the disappearance of such bands.

In both cases, the change in terms of intensity can be considered sufficient to reflect the first signs of the beginning of the polymeric chain scission and chain breaking. Such structural modifications are certainly attributed to aging effect. This result confirms again the mechanical degradation described in [Para 3.3] as well as the harmful effect that plays the immersion aging at different temperatures.

Wave number (cm^{-1})	Functional groups	Type of vibration	Ref.
719 and 730	CH_2	Rocking deformation	[3,14,15]
1117	$\text{C}=\text{O}$	$\text{C}=\text{O}$ stretching	[16]
1462 and 1472	$-\text{CH}_2-$	Bending deformation	[16]
1715	$(\text{RR}') > \text{CO}$	$\text{C}=\text{O}$ stretching where R and R' are aliphatic groups	[15]
	1738	$\text{R}-\text{CO}-\text{OR}'$	$\text{C}=\text{O}$ stretching where R and R' are alkyl groups
		2848	CH_2 symmetric stretching
2916	CH_2	CH_2 asymmetric stretching	[3,15]
3400	$\text{O}-\text{H}$	Water molecules	[3]

TAB. 2 – Spectral FTIR bands studied.

	HDPE immersed	Intensity increase generated		Intensity decrease transformed	Unchanged groups (cm^{-1}) intensity
		up to 1080 Hr at	groups (cm^{-1})		
25°C	719, 1117, 1472, 2916			730, 1600, 1715, 1738, 2848	1161, 1368, 1462,
40°C	719, 965, 1117, 1161, 1368, 1462-1472, 1600,		3400	730, 2848	1715, 1738, 2916, 3400
	60°C		719, 730, 1117, 1161, 1368, 1462-1472, 1600,		2848
					1738, 1750, 2916, 3400

TAB. 3 – Characteristic spectral bands corresponding to generated groups, transformed groups or unchanged groups as a function aging temperature.

up to 1080 Hr at	HDPE immersed												
	719	730	1049	1117	1161	1368	1462	1472	1600	1715	1738	2848	2916 3405
25°C	++	--	+	+	Inv	Inv	+	+	-	w	-	-	w
40°C	+	-	+	++	+	+	+	+	+	++	+	-	w
60°C	+	+	+	++	+	+	+	+	++	+	++++	-	Inv
													+

Inv: invariant; +: increase; -: decrease; w: weak increase.

TAB. 4 – Variation of spectral bands (cm^{-1}) due to chain breaking and chain branching for different aging temperatures.

3.3 Mechanical properties

In this section, the aging impact on some of the mechanical properties of the HDPE has been investigated. These results are shown in FIG. 5, with each mechanical property being represented by the average of three tests.

FIG. 5 shows the variation of the stress versus the strain of the studied material tested in different conditions. As shown in FIG. 5, all stress–strain curves display similar characteristics. They show an initial elastic portion, followed by a drop in stress at the yield point accompanied by the onset of necking. Then the HDPE samples tended to draw and strain hardens up to break of its original gauge length.

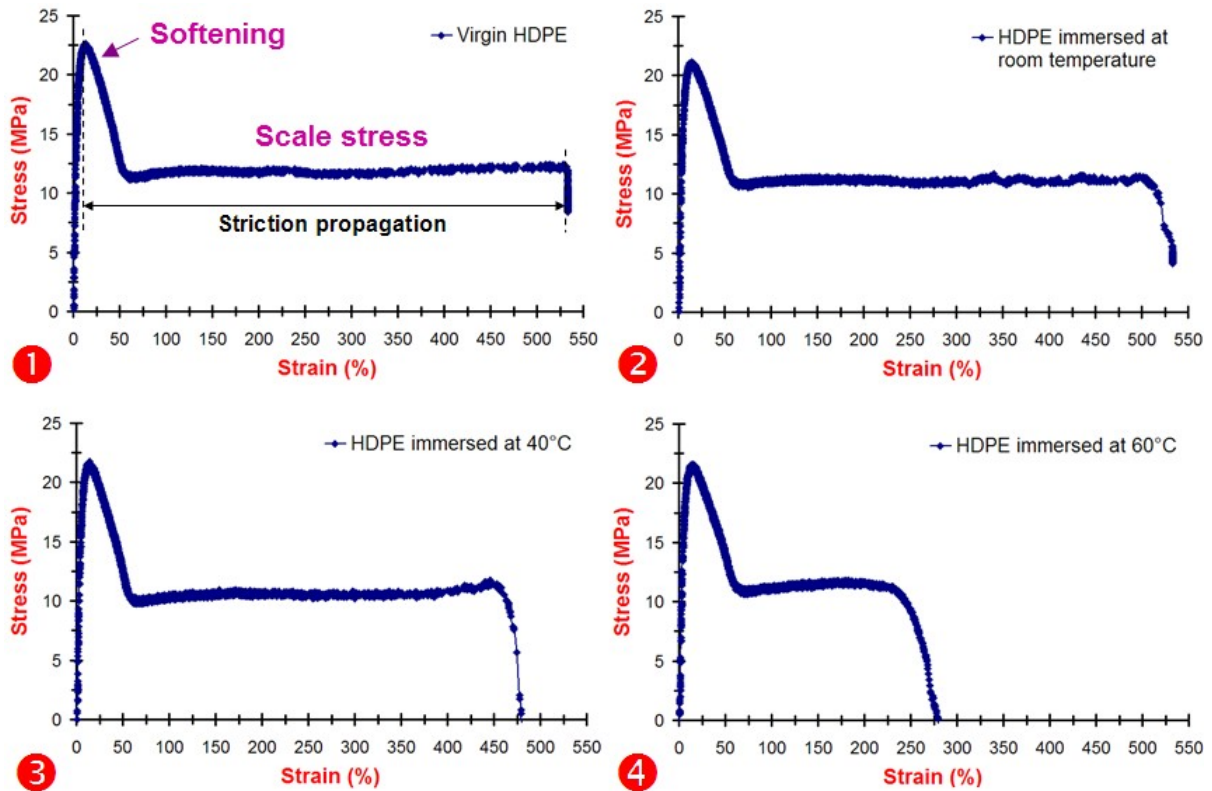


FIG. 5 – Effect of aging temperature on tensile curves of specimens HDPE: unaged (1) aged at 25 (2), aged at 40 (3) and 60°C (4), for 92 days of immersion in the acid H_2SO_4 (pH=1)

As shown in FIG. 6, as the aging proceeds, the four HDPE samples such as virgin and aged in acid at 25°C, 40°C and 60°C. The elongation of the specimens aged at 40 and 60°C is decreased (FIG. 6). The higher the aging temperature increases over the loss of elasticity increases.

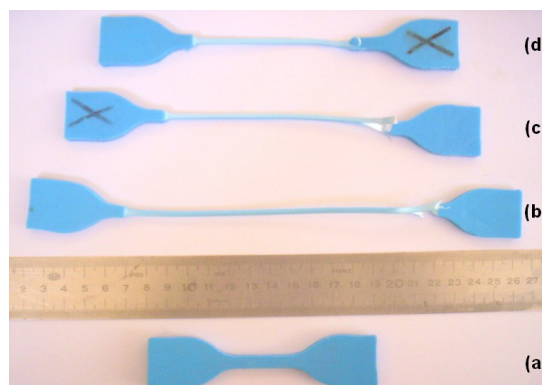


FIG. 6 – Virgin HDPE sample (a). HDPE samples aged in H_2SO_4 : at 25 (b), 40 (c) and 60°C (d) after tensile.

Consistent with the results found in the literature [9,10], such mechanical degradation may be explained by the penetration of the solvent into the polymer structure. In fact, the diffusion of solvent molecules especially in the amorphous phase increases the flexibility of polymer molecular chains [11,12]. Therefore, a plasticization phenomenon takes place during immersion periods [13]. This phenomenon has been already

proved in the previous work [5] by decreasing the glass transition temperature (T_g) for immersion aged samples. All these considerations lead to a decrease in mechanical properties of polymer.

Equally, it is clearly shown that the aging temperature influences the level of the mechanical degradation: higher is the aging temperature, more important is the mechanical degradation. This result may be correlated with the previous paragraph: the immersion behaviour of the studied HDPE depends largely on the aging temperature: an increase of this parameter can lead to accelerate the physical and structural changes which can take place during the immersion process.

Consequently, the mechanical properties are more and more affected as the aging temperature increases.

The mechanism of plasticization, which is generated by the diffusion of the solvent molecules into the amorphous phase of the polyethylene, can also be responsible for such degradation.

4 Conclusion

The sorption phenomenon was investigated, and the diffusion of water molecules into the HDPE sample largely depends on the aging temperature. It was also shown that this factor affects the mechanical response of the studied material in terms of strain and stress at break. Decreases of such mechanical properties as function of aging temperature were also observed.

The structural modifications and chemical changes occurring in the HDPE polymeric chains. Mechanisms intervening in degradation are the following:

- Chain breaking caused by homolytic and heterolytic dissociation.
- Branching and cross-linking formed by radicalary addition.
- Oxidative phenomena.

With respect to the mechanical properties, it must be emphasized the stiffness of the sample as the temperature aging increase by. These mean a decrease of stress at break and, above all, a decrease of the strain at break. The conclusion is then drawn that the major chemical change caused by loss of elasticity and the deformation capacity is manifested in the appearance of carbonyl groups in the core of the polymeric structure.

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