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Creep Behavior of High Density Polyethylene after Aging in Contact with Different Oil Derivates

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The creep behavior of a high density polyethylene (HDPE), currently used as raw material for pipe manufacture, was evaluated before and after exposure to oil derivates using transient rheometry. The creep behavior of the original HDPE was satisfactorily described using a generalized Kelvin-Voigt model based on two retardation times. The values of these critical times were quite different from each other, indicating a large distribution of macromolecular weight. The aging procedure was performed by immersing the polymer in two model fluids chosen to discriminate and understand the action of aromatic and paraffinic fractions of fuel derivatives (white oil, gas-oil). The batch operation was also carried out at two different temperatures to investigate the thermal activation of plausible degrading mechanisms. In the case of the aging performed in the paraffinic fluid, the polymer compliance continuously increased with the immersion duration. This behavior was attributed to a plasticization induced by the diffusion of the liquid in the polymer matrix. The same phenomenon was observed in the early stage of the HDPE aging carried out with the aromatic fluid. However, for longer aging times, the extraction of low molecular weight species produced the stiffening of the thermoplastic. POLYM. ENG. SCI., 00:000-000, 2010. © 2010 Society of Plastics Engineers

INTRODUCTION

Carbon steel is the main material used to manufacture pipelines used for transportation of gas, oil and its derivatives. However, this material has at least two main drawbacks, namely: corrosion and a fairly high internal roughness [1]. Corrosion can severely reduce the integrity of

the pipeline network while the internal roughness of steel pipes contributes to the flow reduction of fluids that are transported. Therefore, the substitution of old steel transportation grids by new ones using polymers or steel tubes with an inner polymeric layer instead of an all-steel pipe is a common trend since polymers are corrosion resistant and can also be manufactured with very small surface roughness.

High density polyethylene (HDPE) is a natural choice due to its good properties, its large availability, and its reduced cost. However, it is well known that polymers can present either physical and/or chemical aging when exposed to aggressive environments like those found when gas and oil derivatives are considered [2]. Different phenomena were already reported in the literature about the failure of HDPE pipes. Swelling, microcracks and plasticization are common problems related to the aging of polymers [3, 4]. According Ward et al. [5], the different mechanisms can often coexist in HDPE due to the semicrystalline morphology of the polymer. As a consequence, it is often pertinent to combine several experimental techniques to investigate the physicochemical behavior of HDPE in harsh environment. For a safe use of polymer pipelines, it is crucial to know the evolution of the mechanical behavior of the polymer in severe conditions of use. Creep measurements seem to be an excellent method to analyze the evolution of the viscoelastic properties and more particularly when the load-bearing capacity of a plastic product is essential for the final application.

Several empirical approaches have already been proposed in the literature to describe the long-term mechanical performances of polymers. As regards the creep response, the Kohlrausch-Williams-Watts relation is often used to fit the experimental data get with many thermoplastics materials. But, the KWW equation is only applicable for creep conducted over limited periods of time and for low strain values [6]. Nevertheless, the

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well-known time-temperature superposition principle can be used to extend the time domain of the creep response. For thermorheologically simple polymers, the method consists in registering the creep compliance at different temperatures over short durations. Then, a more complete curve equally named master curve, can be built on a larger time scale by horizontal shift of the experimental series along the time axis. The shift factor obeys to the William-Landel-Ferry (or WLF) equation [7]. In fact, this method is relevant with many amorphous polymers but is not appropriate with semicrystalline thermoplastics for which the time-temperature superposition principle is not valid [8].

The creep behavior of HDPE is often reported as being nonlinear because of the coexistence of amorphous regions with crystalline phase. For some authors, the dependence of the HDPE compliance with the applied stress can be described using the Leaderman model that is based on the separation of the stress and time functions [9, 10]. Different models tried to relate the nonlinear creep of a polymer with molecular mechanisms. One of the most successful methods is derived from free-volume theory. It is supported by the fact that the creep behavior of a polymer is influenced in a similar way by an increase of the mechanical stress and a reduction of the temperature [11]. Another interesting methodology used with HDPE is based on the “material clock” concept. This approach considers that the creep response is controlled by an internal time of the polymer which differs from laboratory observation time. The discrepancy between both times is due to the current state of the material and is dependent on several quantities such as free volume, strain or stress [12].

As a matter of fact, if several authors have already investigated the characteristics of HDPE creep behavior, a much smaller number of studies dealt with the changes induced by the exposure to oil derivatives. Sakata et al. conducted various researches about the degradation mode of polyethylene after exposure to fuel oil. Unfortunately, the aging temperature used to accelerate the plausible degradation mechanism was excessive compared to the conditions used for the transportation of oil derivatives [13, 14]. Indeed, in these studies, the material was exposed up to $T = 430^{\circ}\text{C}$, temperature for which the polymer was in the molten state and even able to degrade according pyrolytic process.

This whole scientific framework encouraged the conduction of our work devoted to the characterization of the creep behavior of a HDPE grade, used to manufacture pipes. In this way, we mainly wished to analyze and interpret the consequences of the polymer exposure to two different fluids, chosen to model the physicochemical action of oil derivatives for periods of aging up to 5 months. To have a better understanding of the mechanisms at the origin of the changes in the rheological response, gravimetric measurements were performed on the same HDPE grade and for the different aging conditions.

EXPERIMENTAL

Polymer Matrix

A commercial HDPE pipe used for the transportation of gas and other fluids was provided by Brastubo Company (Brazil). To make possible the conduction of rheological tests in the solid state, the polymer tube was remolded in rectangular samples (2 mm thick, 10 mm large, and 40 mm long) using a heating press. According manufacturer’s specifications, the specimens were prepared using a molding temperature set at $T = 210^{\circ}\text{C}$ and a pressure $P = 10$ bars maintained constant during $t = 10$ min. This overall procedure was judged preferable to the direct cutting of the tube for two main reasons: (i) the rheometer required samples that were perfectly flat, (ii) a mechanical cutting could engender artificial defects such as microcracks that would certainly affect the material behavior versus fluids.

Model Fluids

Oil derivatives are comprised with a large variety of chemical species that can roughly be classified either in aromatic or paraffinic units [15, 16]. To discriminate the action of each elementary compound, the use of model fluids is often very interesting. This option was retained in this work since HDPE samples were aged using two different model liquids. The first one, named Marcol 52[®] was purchased from Esso Company. It is generally named as “white oil” in petroleum industry and is known to be quite rich in paraffinic units. The second model fluid is gas-oil as classically found in commercial distribution network. Both fluids were used without any further purification.

Aging Procedure

The polymer was aged by immersion of the different specimens into the two model fluids for periods up to 150 days. To investigate the activation of the aging phenomena, two aging temperatures were selected: 25 and 50°C . The highest one, chosen far away from the polymer degradation temperature, was used to accelerate the degradation mechanisms and make it possible their observation at shorter times than at the ambient.

Gravimetry

The diffusion of the liquid into the polymer matrix was quantified with gravimetric measurements. The methodology consisted in measuring the samples weight after immersion in a model fluid (gas-oil or Marcol) and using a high precision microbalance (10^{-4} g). The results were plotted as the evolution of the relative weight change ΔM_t as a function of the immersion time t :

$$\Delta M_r = \frac{M(t) - M_i}{M_i} \quad (1)$$

where M_i is the initial weight of a polymer sample and $M(t)$ the value measured after immersion in a model liquid during a period of time t .

Rheometry

The thermomechanical behavior of the initial HDPE was determined as a function of temperature using a stress-controlled rheometer (AR2000 from TA Instruments) equipped with a rectangular torsion geometry. The experiment is based on the determination of the complex shear modulus $G^* = G' + jG''$ of the polymer. The component G' , called “storage modulus,” represents the mechanical rigidity of the sample whereas G'' relates to the dissipated mechanical energy. The apparatus was also equipped with an environmental testing chamber that allowed temperature control from -150°C up to the polymer melting point with a heating ramp of $3^\circ\text{C}/\text{min}$. In this kind of experiment, the imposed stress σ was sinusoidal (dynamic mode) with a shearing angular frequency ω set to 10 rad/s but its amplitude was unchanged during the test ($\sigma = 10^5$ Pa). This value was chosen in a domain where the rheological response of the polymer was not affected by the stress value.

The creep behavior of the original and aged polymeric specimens was studied using the same rheometer but in transient mode: the imposed stress does not evolve anymore with time according a sinusoidal function but is maintained at a precise value (= step function) and the resulting strain of the sample is simultaneously measured while the temperature is kept constant. To fully characterize the initial polymer, creep tests were performed at four different temperatures (30, 50, 100, and 120°C), and at six stress levels (5, 10, 50 kPa, 0.1, 0.5, and 1 MPa). After aging, the creep behavior of the soaked specimens was determined in the same stress range as used for the rheological characterization of the initial polymer. For clarity, only the most pertinent results were presented. The testing temperature was set at a mild temperature of 30°C that is characteristic of the conditions often encountered in the transportation and the distribution of several oil derivatives. Please note that some experiments performed at higher temperatures ($T = 70^\circ\text{C}$) provoked partial evaporation of the model fluids during the test. This brought undesirable modifications of the phenomena under analysis (poor reproducibility, no-sense evolution. . .) and was quite marked in the case of gas-oil.

RESULTS AND DISCUSSION

Characterization of the Original HDPE

Figure 1 depicts the results of the thermomechanical analysis of the initial HDPE. As expected, the overall profile is characteristic of a semicrystalline polymer. In the

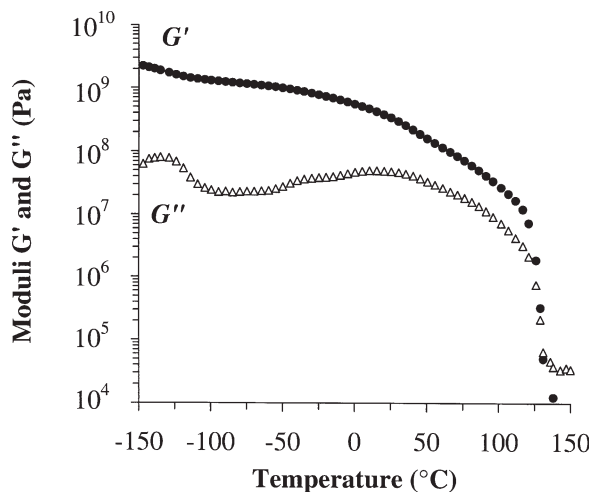


FIG. 1. Thermomechanical analysis of the original HDPE at $\omega = 10$ rad/s. G' (■) and G'' (Δ).

low temperature region, the thermoplastic presents a high mechanical rigidity ($G' > 10^9$ Pa). Then, at $T = -128^\circ\text{C}$, the curve of the elastic modulus G' shows a deflection while the G'' curve presents a relaxation peak. These phenomena are characteristic of the mechanical relaxation of the amorphous phase during the glass transition of the polymer. For higher temperatures, the values of the G' and G'' slightly decrease with temperature up to $T = 120^\circ\text{C}$ due to the persistence of the crystalline regions. Above $T = 125^\circ\text{C}$, the softening of the crystalline phase is in turn observed. In other words, the polymer is in the molten state.

To further characterize the rheological properties of the polymer before aging, creep tests were undertaken. From the measurement of the sample strain as a function of the time, it is more common to plot the variation of the compliance $J(t)$ defined by [7]:

$$J(t) = \frac{\gamma(t)}{\sigma_0} \quad (2)$$

where σ_0 is the applied stress. Figure 2 shows the results of the creep analysis conducted on the original HDPE for different values of applied stress and at $T = 30^\circ\text{C}$. One can observe that all the curves tend towards a limit value when $t \rightarrow \infty$. This evolution is characteristic of the rheological profile classically observed with a viscoelastic solid. At the lowest values of the applied stress, i.e. when $\sigma_0 \leq 0.1$ MPa, the compliance curves can be superimposed. In other words, the mechanical behavior of the polymer is little influenced by the applied stress. In this stress range, the rheological behavior of the polymer is said to be linear since the strain $\gamma(t)$ evolves versus the imposed stress σ_0 according a linear function so that the compliance is constant [17]. The limit value J_∞ get at highest times allows the determination of the shear modulus of the polymer $G = 1/J_\infty = 1.5 \times 10^8$ Pa at $T = 30^\circ\text{C}$. This value

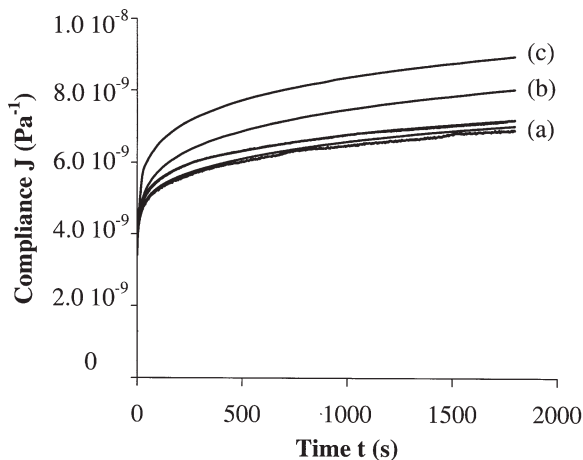


FIG. 2. Compliance curves of the original HDPE registered at $T = 30^{\circ}\text{C}$. Series (a): $5 \text{ kPa} \leq \sigma_0 \leq 0.1 \text{ MPa}$. (b): $\sigma_0 = 0.5 \text{ MPa}$. (c): $\sigma_0 = 1 \text{ MPa}$.

agrees with that usually observed for this class of polyolefin in the same temperature range [18–21]. It is also in concordance with the magnitude of the shear modulus $|G^*| = \sqrt{G'^2 + G''^2}$ at $T = 30^{\circ}\text{C}$ that can be calculated from thermomechanical data previously shown in Fig. 1. For larger stress values, that is to say $\sigma_0 > 0.1 \text{ MPa}$, the creep behavior is more affected by the value of the applied stress: the viscoelastic response of the original HDPE is now nonlinear as often reported in the literature [9–12].

The same general behavior was observed when the creep tests were performed at higher temperatures (50, 100, and 120°C). Figure 3 shows the compliance curves obtained when the tests were conducted at 120°C . The other results are not shown here for the sake of shortness. From the compliance curves obtained at the several testing temperatures, it was found that the critical threshold dividing the linear and nonlinear rheological behavior of the initial HDPE was not very strongly affected by the

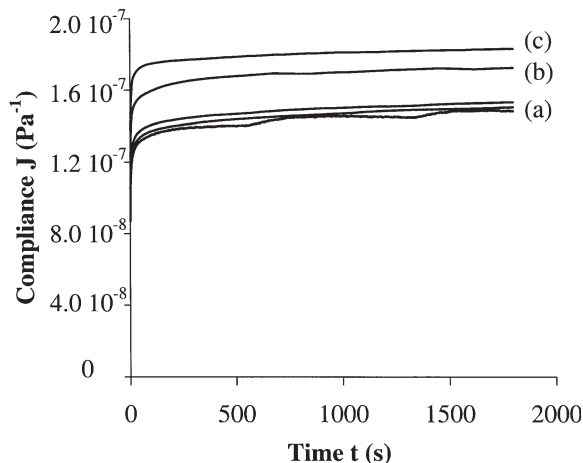


FIG. 3. Compliance curves of the original HDPE at the temperature $T = 120^{\circ}\text{C}$. Series (a) $10 \text{ kPa} \leq \sigma_0 \leq 0.1 \text{ MPa}$. (b) $\sigma_0 = 0.5 \text{ MPa}$. (c) $\sigma_0 = 1 \text{ MPa}$.

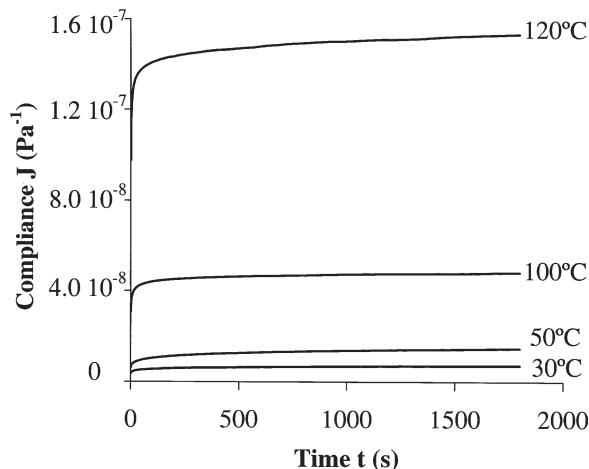


FIG. 4. Influence of the testing temperature on the evolution of the compliance as a function of the time and at the imposed stress $\sigma_0 = 0.1 \text{ MPa}$.

testing temperature. However, at the same value of the imposed stress, the compliance value increases as the test temperature is raised revealing a higher mechanical flexibility provoked by enhanced chain mobility. Figure 4 illustrates this aspect for the HDPE samples submitted to a constant stress ($\sigma_0 > 0.1 \text{ MPa}$) at various temperatures. The reduction of the mechanical rigidity G (calculated as the inverse of J_{∞}) is important when the temperature is close to 120°C because of the vicinity of the polymer melting point (see Fig. 5). These data present a good concordance with G' values registered with the thermomechanical analysis of the polymer as previously shown in Fig. 1.

It is well established that the rheological behavior of polymers can be described using analytical models based on the series and parallel association of elastic and viscous elements [7, 22]. This approach is undeniably simple if it is compared with more developed concepts based on

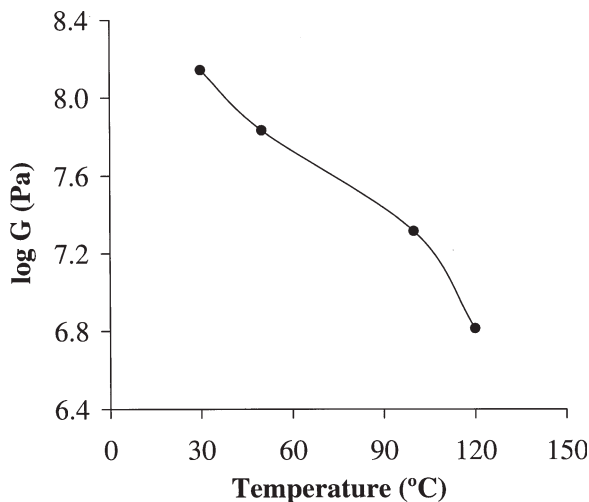


FIG. 5. Effect of the temperature on the mechanical rigidity of HDPE deduced from compliance data (the line is given as a guide).

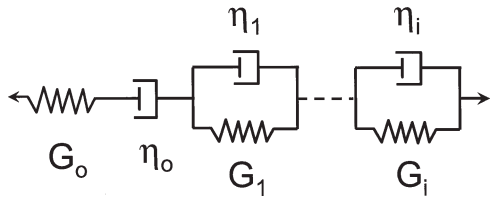


FIG. 6. Representation of the generalized Kelvin-Voigt model.

structural or molecular aspects and that were briefly presented in introductory part. Anyway, the generalized Kelvin-Voigt model which is represented in Fig. 6 was found to give reliable results in this work. This analogical model is made by the association of springs and dashpots. Each spring is characterized by an elasticity G_i and the dashpot by a viscosity η_i . For the creep test, where $\sigma = \text{constant}$ and $\gamma = f(t)$, the equation defining the compliance of the polymer for this model is:

$$J(t) = J_0 + \frac{t}{\eta_0} + \sum_{i=1}^n J_i(1 - e^{-t/\theta_i}) \quad (3)$$

where J_0 is the instantaneous compliance, i.e., at the moment of loading $t = 0$ and η_0 is the polymer viscosity. θ_i is the retardation time of the i th parallel association ($\theta_i = \frac{\eta_i}{G_i}$).

When a solid polymer is under analysis, the influence of the first dashpot can be disregarded, considering that it has a very large viscosity ($\eta_0 \rightarrow \infty$). Therefore, Eq. 3 can be rewritten as

$$J(t) = J_0 + \sum_{i=1}^n J_i(1 - e^{-t/\theta_i}) \quad (4)$$

The simplest situation is attained for this model when just one parallel element is in series with the elastic (spring) element, i.e., when $i = 1$. Therefore,

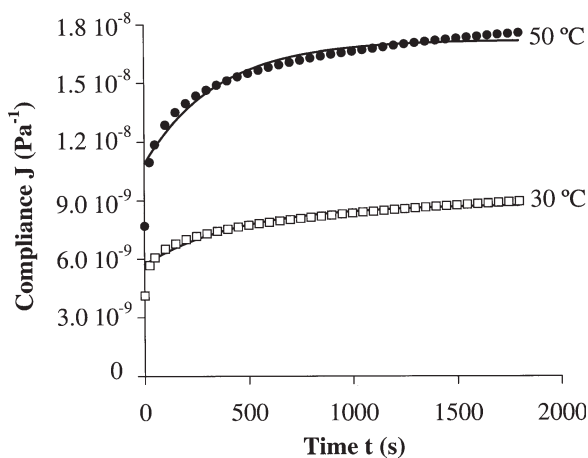


FIG. 7. Adjustment of the original HDPE compliance versus time using the generalized Kelvin-Voigt model with one retardation time (solid line). Experimental data (\square : 30 °C - \bullet : 50 °C) registered at $\sigma_0 = 1$ MPa.

TABLE 1. Parameters of the generalized Kelvin-Voigt model with one retardation time. Data for $\sigma_0 = 1$ MPa.

Temperature (°C)	J_0 (Pa ⁻¹)	J_1 (Pa ⁻¹)	θ_1 (s)
30	5.71×10^{-9}	3.10×10^{-9}	466
50	1.09×10^{-8}	6.32×10^{-9}	355
100	4.87×10^{-8}	6.20×10^{-9}	308

$$J(t) = J_0 + J_1(1 - e^{-t/\theta_1}) \quad (5)$$

Figure 7 shows the plot of the experimental points for the HDPE compliance registered at $\sigma_0 = 1$ MPa and at two test temperatures. By numerical fitting, we have determined the best values of the three parameters J_0 , J_1 , and θ_1 to fit the curve using Eq. 5. The adjusted curves are represented on the same Fig. 7. One can note that the analogical model allows a quite satisfactory prediction of the experimental data except in the initial part of the curves. The set of adjusted values obtained are listed in Table 1.

However, better results can be obtained if Eq. 5 is expanded to contain two retardation times. Namely,

$$J(t) = J_0 + J_1(1 - e^{-t/\theta_1}) + J_2(1 - e^{-t/\theta_2}) \quad (6)$$

An example showing the comparison of the adjusted curves using Eqs. 5 and 6 is shown in Fig. 8. Table 2 lists the values of the parameters obtained for the creep test performed at $T = 30^\circ\text{C}$ and under an imposed stress of 1 MPa. One can see that the two retardation times are very different from each other and differ from the value obtained when the generalized model is based on an only retardation time, Table 1. In fact, the value obtained when Eq. 5 was used falls between those found when Eq. 6 is used.

The better fitting obtained with Eq. 6 and the fact that both retardation times have very different values is an indication that the HDPE analyzed presents a large distribution of molecular weight. Smaller retardation times are

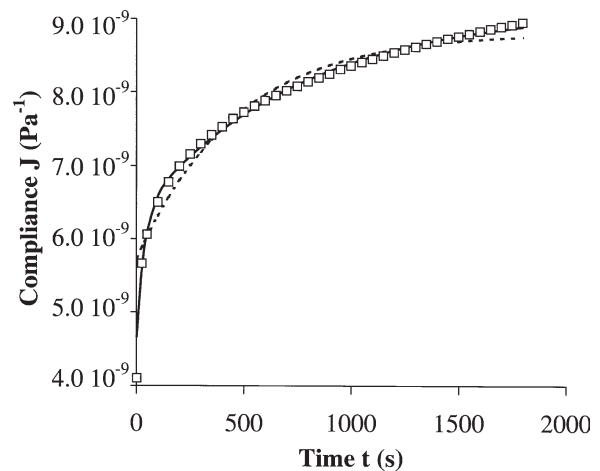


FIG. 8. Comparison of the fittings of the experimental compliance curves (\square) with the generalized Kelvin-Voigt model with one (dotted line) and two retardation times (solid line) at $T = 30^\circ\text{C}$.

TABLE 2. Parameters of the generalized Kelvin-Voigt model with two retardation times when $\sigma_0 = 1$ MPa.

Temperature (°C)	J_0 (Pa ⁻¹)	J_1 (Pa ⁻¹)	J_2 (Pa ⁻¹)	θ_1 (s)	θ_2 (s)
30	4.61×10^{-9}	1.74×10^{-9}	2.82×10^{-9}	36.2	773

characteristic of low molecular weight macromolecules whereas, higher retardation times are specific of high molecular weight chains [23]. The large distribution of molecular weight of this polymer was confirmed by the master curve obtained from various spectromechanical characterizations undertaken at different temperatures. Indeed, a Havriliak-Negami model based on a distribution of retardation times, was required to satisfactorily model the polymer viscoelastic behavior as a function of the shearing frequency [24].

To our knowledge, such distribution of molecular weight in HDPE is often used for the manufacture of plastic pipes. Indeed, it allows the production of pieces with very good mechanical properties. In particular, the impact strength, the stiffness and the tensile strength are significantly improved. On the long term, this kind of polymer is also characterized by a good resistance to stress cracking. At least, the processability is also easier what can be related to the fact that the polymer chains with low molecular weight act as a plasticizer [25–28].

Study of the Aged Material

Figure 9 depicts the relative weight variation of the polymer samples as a function of aging time and for the different immersion fluids at the temperature $T = 25^\circ\text{C}$. The liquid diffusion into the polymeric matrix can be observed in both cases since the sample weight significantly increases with immersion time. Nevertheless, the HDPE affinity is much higher with gas-oil than with Marcol. Indeed, with the aromatic fluid, the weight increase is faster and the saturation point is observed after 30 days of aging. In the case of Marcol, the equilibrium is not reached even after 150 days of immersion.

Figure 10 shows that the same hierarchy between the fluids is obtained at higher temperature ($T = 50^\circ\text{C}$). But, the diffusion process is indisputably more pronounced and quicker at this latter temperature. For instance, the saturation points are respectively observed after 15 and 44 days for the immersions conducted in gas-oil and Marcol. The same data also show an interesting phenomenon in the case of HDPE aging performed in gas-oil. For long periods of time, the sample weight decreases after reaching the saturation limit. In fact the same phenomenon was already present on the gravimetric curve of the HDPE aged in gas-oil at 25°C but at a lower extent. Two hypotheses could explain the reduction of the relative weight: i) this peculiarity is characteristic of a fluid desorption or ii) it is due to the extraction of chains with low molecular weight by the immersion liquid. The results of the creep experi-

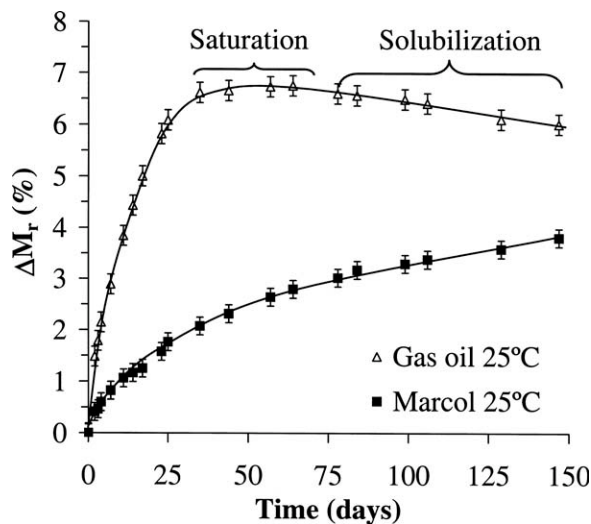


FIG. 9. Variations of the relative weight of HDPE as a function of the immersion time for both model fluids at $T = 25^\circ\text{C}$.

ments detailed hereafter will be useful to discriminate which hypothesis is valid.

Figure 11 shows the evolution of the HDPE compliance after exposure to the aromatic model fluid at 25°C . The different curves related to variable aging times were registered under a stress of 0.5 MPa. The rheological response of the initial HDPE is also shown for easier comparison. It can be seen that for shorter aging times, a significant increase of the compliance occurs what reveals that the HDPE is plasticized after exposure to gas-oil. This peculiarity is reliably due to the diffusion of the aromatic liquid in the polymer matrix as previously shown by the gravimetric measurements [29, 30]. However, for longer aging times ($t > 100$ days) the increase of the compliance is more limited and seems to point out that the plasticizing effect is less important. It is worthy of

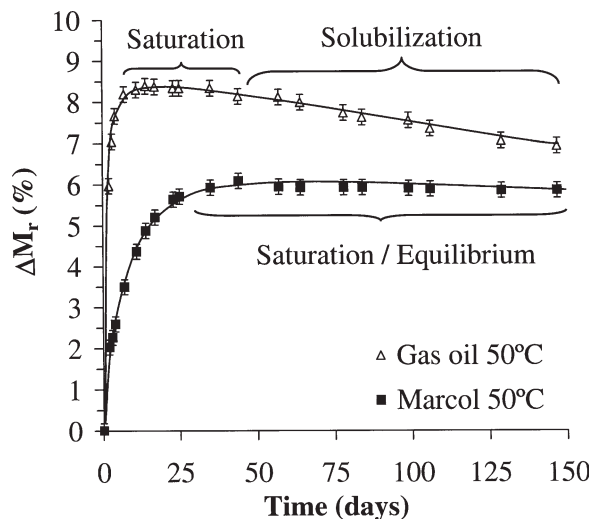


FIG. 10. Evolution of the relative weight of aged HDPE as a function of the immersion time for both model fluids at $T = 50^\circ\text{C}$.

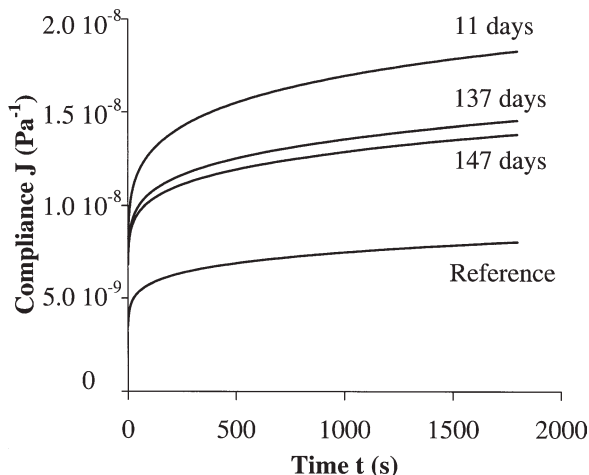


FIG. 11. Effect of the aging time on the creep behavior of HDPE after immersion in the aromatic model fluid at $T = 25^{\circ}\text{C}$ ($\sigma_0 = 0.5 \text{ MPa}$).

note that this phenomenon occurs for aging times for which the gravimetric curves decrease after the saturation point. Then, this aging period can be reasonably interpreted as being characteristic of the solubilization and extraction of low molecular weight chains. Indeed, low molecular weight chains represent natural plasticizing units in the polymer matrix. Their removal provoked by aging in the model aromatic fluid is logically at the origin of the reduction of the HDPE flexibility.

The results of the creep tests performed on the polymer aged in the same aromatic fluid but at $T = 50^{\circ}\text{C}$ seem to assess the validity of previous mechanisms. Obviously, at this higher aging temperature, the beginning of the stiffening process due to solubilization and extraction of the low molecular weight segments was found to occur at earlier times, due to the well known temperature dependence of the diffusion/aging process [2]. Once more, it occurs after the saturation point that is to say for an aging time exceeding 44 days. The corresponding zone on the gravimetric curve is characterized by a decrease of the relative weight of the aged sample with the immersion time.

Figure 12 proposes a direct comparison of the HDPE creep curves for both aging temperatures in gas-oil. For the shorter times, the liquid diffusion in the polymer matrix and consequently the HDPE plasticization, are accelerated by temperature. Then, the compliance of the polymer aged at 50°C is higher than that of the polymer aged at 25°C (see Fig. 12). For longer aging times, the solubilization and extraction occur. As they are thermally activated, they produce themselves at a higher extent in the HDPE aged at 50°C in comparison of the sample aged at 25°C during the same period of time (i.e., 137 days of immersion). As a result, the compliance of the polymer aged at $T = 50^{\circ}\text{C}$ is smaller than that observed for at $T = 25^{\circ}\text{C}$ (see Fig. 13). In other words, the stiffening of the thermoplastic is higher for the sample aged at high temperature in gas-oil.

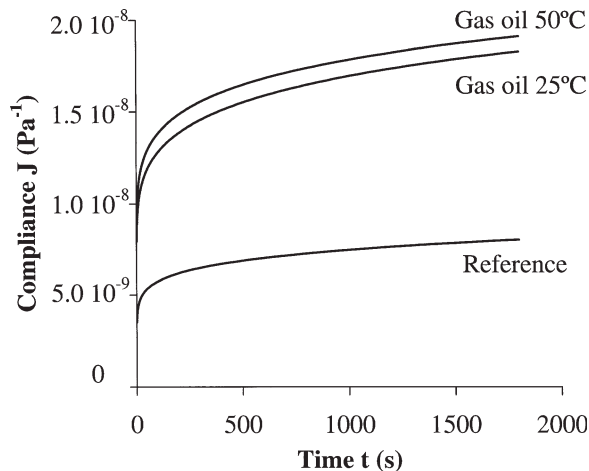


FIG. 12. Influence of the aging temperature upon HDPE plasticization after exposure to the aromatic fluid (aging time = 11 days— $\sigma_0 = 0.5 \text{ MPa}$).

The mechanisms at the origin of the HDPE aging in the other model fluid (Marcol) were easier to interpret. As detailed before, the gravimetric section showed a regular increase of weight of immersed sample due to diffusion of the paraffinic fluid in the polymer matrix. Obviously, this phenomenon affects the creep behavior of the aged HDPE. Figures 14 and 15 clearly illustrate that the polymer compliance continuously increases with the aging time and any of the aging temperature considered. Once more, the plasticization is activated by the temperature since it produces itself at a higher extent. No future tendency to stiffening was registered even for long periods of aging time.

CONCLUSIONS

This article first dealt with the creep behavior of the original HDPE. Two rheological regions were identified

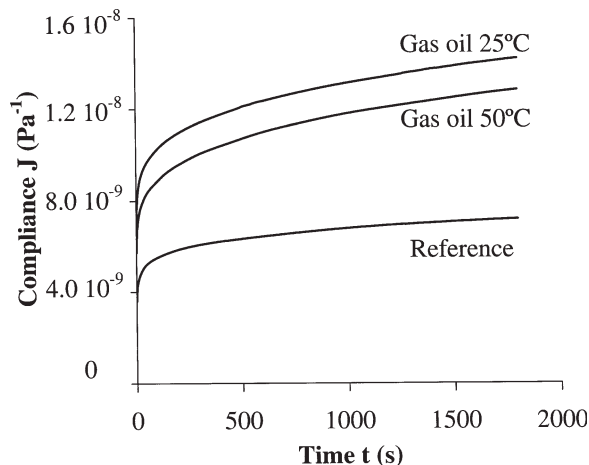


FIG. 13. Influence of the aging temperature upon HDPE stiffening due to the prolonged exposure to the aromatic fluid (aging time = 137 days— $\sigma_0 = 0.1 \text{ MPa}$).

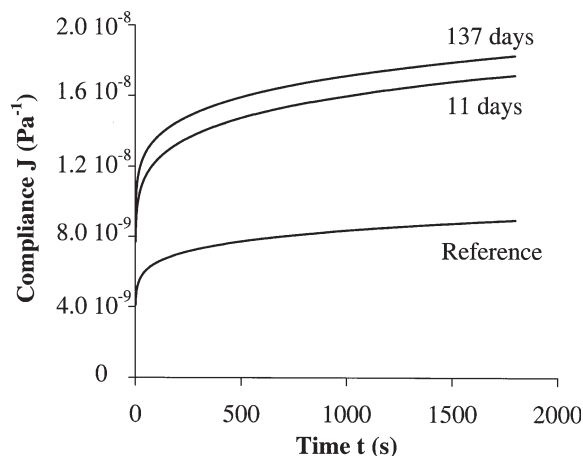


FIG. 14. Creep behavior of HDPE after exposure to the model paraffinic fluid at $T = 25^{\circ}\text{C}$.

as a function of the stress applied, namely: (i) a linear rheological domain when $\sigma_0 \leq 0.1$ MPa; (ii) a nonlinear rheological behavior when $\sigma_0 > 0.1$ MPa. In the solid state, that is to say for $T < 125^{\circ}\text{C}$, the temperature does not affect the threshold separating the linear and nonlinear rheological domains.

The best fitting of the creep properties of the original HDPE was obtained using the Kelvin-Voigt model based on two retardation times. The large difference between the values of the retardation times was judged as a reliable indication that the material under analysis presented a large distribution of molecular weight.

Transient rheometry was quite useful to investigate the effects of HDPE exposure to different oil derivatives. The creep behavior of the polymer showed an important evolution after immersion of the thermoplastic in the model fluids for variable periods of time and at different temperatures. When aging was performed with the paraffinic model fluid, the compliance continuously increased revealing the plasticization of the polymer. On the basis

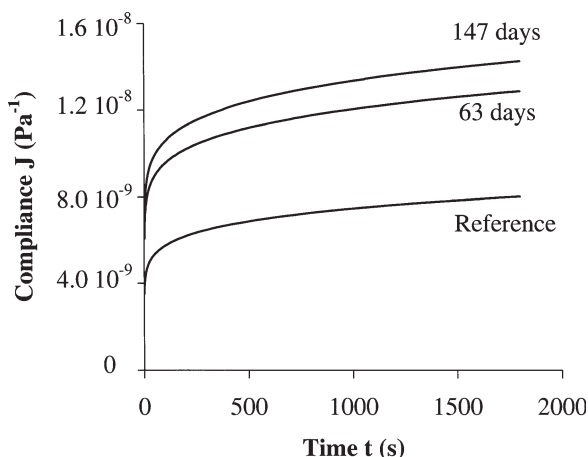


FIG. 15. Creep behavior of HDPE after exposure to the model paraffinic fluid at $T = 50^{\circ}\text{C}$.

of gravimetric measurements, this phenomenon was related to the liquid diffusion in the polymer matrix. In the case of the samples aged in contact with the aromatic model fluid, more complex phenomena were described. For short aging times, the polymer plasticization is observed again. But, for longer immersion times, the solubilization and extraction of low molecular weight species induced a progressive stiffening of the polymer. Then, in the industrial application (pipe for oil transportation), one has to keep in mind that the mechanical behavior of the polymer will not be stable. This latter point is important for the reliability prediction of the network transportation and distribution.

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