

Ageing of Polyamide 11 Used in the Manufacture of Flexible Piping

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ABSTRACT: The influence of temperature and pH on the ageing of piping made from polyamide 11 (PA-11) was studied using water from an oilfield (pH = 5.5) and deionized water (pH = 7.0) with monitoring by corrected inherent viscosity (CIV) measurements. The hydrolytic degradation was more extensive at high temperatures in oilfield water. When the system reaches equilibrium, the pH affects mainly the CIV plateau values. Thermogravimetry, energy-dispersive X-ray spectroscopy, differential scanning calorimetry, X-ray diffraction, and scanning electron microscopy

measurements were also used to investigate aspects involved in the ageing PA-11. The hydrolytic degradation of PA-11 leads to formation of low molar mass compounds, such as oligomers dispersed in the polymeric matrix. This is a process that occurs preferentially in the amorphous domain of PA-11, which leads to an increase in the degree of crystallinity and the formation of a new γ -phase. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1777–1783, 2009

Key words: ageing; degradation; polyamides; viscosity

INTRODUCTION

Polyamides are polymeric materials used in various applications ranging from household devices, such as clothing, carpets, and stockings, to engineering materials like pipelines, tubes, gears, and automotive components. Extensively studied since first being synthesized by Carothers at DuPont, the great success of these thermoplastics as engineering materials is due to their mechanical strength, high elasticity, and high melting point.¹ These properties are attributed to molecular interactions involving the amide group (—CONH) which also facilitate the penetration of water into the polymeric matrix making the polyamide hygroscopic. The physical and chemical properties of polyamide are directly affected by its ability to absorb water and can be controlled by the number of methylene groups in the backbone of the polymer. Because of that, the study of the degradation of polyamides in ageing tests has become important.^{1–12} Because of the high quantities of

methylene groups in the structure of polyamide 11 (PA-11) in comparison with PA-6 or PA 6-6, PA-11 has become more important in applications in pipes for water-containing fluids.

PA-11 was one of the first polymers used for the internal insulation layers in flexible pipelines used in offshore oilfield exploitation. Its excellent mechanical properties (high fatigue resistance, low frictional coefficient, excellent creep resistance) and good chemical resistance enable the use of this semicrystalline thermoplastic material as a barrier during the transport of the gas, water, and oil mixtures.^{2,13} In addition to varying the quantities of methylene groups as a means of changing polymer properties, plasticizers are also used in flexible pipes to improve flexibility and to reduce hardness. For PA-11, the plasticizer used is *N*-butyl-benzenesulfonamide in 12 wt % concentration.^{2,14}

The main external factors that affect the degradation process of PA-11 pipes are: water contained in fluids, temperature, acidity, composition of the oil, and the presence of other chemical products used for oil treatment. The main properties affected are: loss of plasticizer and therefore elasticity changes in morphology and the reduction of the molar mass due to hydrolysis. The presence of water during the oil production is one of the major factors affecting

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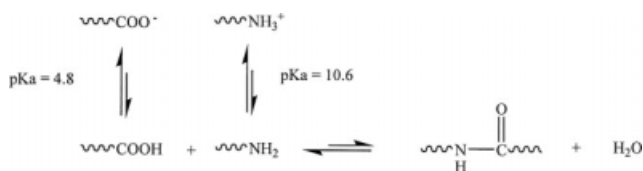


Figure 1 Polycondensation-hydrolysis equilibrium reaction of PA-11.

the ageing of PA-11. The hydrolysis reactions of PA-11 are reversible and are described in the literature.^{4,13} It has also been shown that the hydrolysis rate is exponentially dependent on temperature. The decrease of inherent viscosity (IV) as a function of time of hydrolysis at 90–140°C reaches a plateau which suggests that at this point the system is in a state of equilibrium.² The value of the IV or the molar mass in equilibrium is slightly dependent on temperature.^{2,4,6}

Acids and gases found in oil also play an important role in the PA-11 ageing process. These are mainly inorganic acids, such as carbonic acid and hydrogen sulfide, and to a lesser extent several, organic acids. It has been shown that they catalyze the hydrolysis of the PA-11 when the concentration of water adsorbed in the PA-11 exceeds that of the amine end-groups.^{13,15} When the pH is reduced from 7 to 4, the concentration of ammonium end-groups increases, thereby decreasing the concentration of amine groups and moving the polycondensation-hydrolysis equilibrium to the left (see Fig. 1). Therefore, precise knowledge of the effect of acids on offshore oil and gas production conditions is important to estimate the lifetime of PA-11 pipes.

Oilfield water, which exists naturally in rocks before drilling, contains a variety of dissolved organic and inorganic compounds. This water is the most corrosive element found in the oilfield operations, mainly due to the presence of large quantities of carbon dioxide, hydrogen sulfide, and aggressive salts, such as chlorides and sulfates. The amount of oilfield water used to extract the oil can reach values of the order of 50% by volume produced or even closer to 100% at the end of the productive life of the wells. This as well as other factors, such as temperature, pH, and pressure, accelerate the ageing of the flexible pipes.^{16,17}

Presently, there is a special interest in determining the accurate degradation limit before these polyamide polymers begin to pose risks to the security of offshore installations.^{13,18,19} In the present work, the degradation process was monitored by measuring the IV. As this thermoplastic contains additives, it was necessary to correct the IV.^{2,13} The determination of the content of additives was made through thermogravimetric analysis (TA). Energy-dispersive X-ray spectroscopy (EDS) measurements were

carried out to check the behavior of these polymeric additives during the ageing process. The effect of hydrolysis on the structure and morphology of the material was studied through measurements of X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL SECTION

The samples of PA-11 containing 10–12 wt % *N*-butyl-benzenesulfonamide plasticizer were taken directly from the inner sheath of an unused commercial flexible oil pipe supplied by PETROBRAS S.A./CENPES. Samples were cut to dimensions of 13.0 × 34.5 × 5.5 mm³, set in brackets of stainless steel and submerged in the ageing fluid inside a 2 L reactor with a removable lid. To prevent accidents caused by the expansion of the liquid, 75% of the total volume was used.

Ageing tests were made in deionized water (18.2 MΩ) from a Permutation water purification system. Oilfield water (pH 5.5) from a commercial oil well was also supplied by PETROBRAS S.A./CENPES. To prevent the overlay between oxidative and thermal degradation processes, oxygen was removed from the system by bubbling argon (quality 99.999%) for 3 h in the reactor before the ageing experiments.¹ Fluids were replaced at each sampling step so that the closed system would model as close by possible the behavior of an open system. The ageing tests were performed at different temperatures according to Table I.

Before measuring the viscosity, the samples were dried overnight in a vacuum oven at 80°C, pressure <10² Pa, and equilibrated at room temperature for 15 min. Virgin and aged PA-11 samples were dissolved in *m*-cresol and heated with stirring for 60 min at 100°C to make a sample solution with a concentration of 5.00 ± 0.02 × 10⁻³ g cm⁻³. The viscosity measurements were done using a semiautomatic unit, D15KP-LAUDA, coupled to a thermostatic bath operating at (20.0 ± 0.1)°C. Values of IV for each solution were calculated according to eq. (1) where IV, *t*₀, *t*, and *c* are the IV (dL g⁻¹), the flow time for *m*-cresol, the flow time of the solution (in seconds), and the concentration (g dL⁻¹), respectively.

TABLE I
Immersion Times in Deionized Water and Oilfield Water

Reaction environment	Temperature (±3°C)	Total immersion time (days)
Deionized water	110	50
	120	50
	140	30
Oilfield water	120	50
	140	30

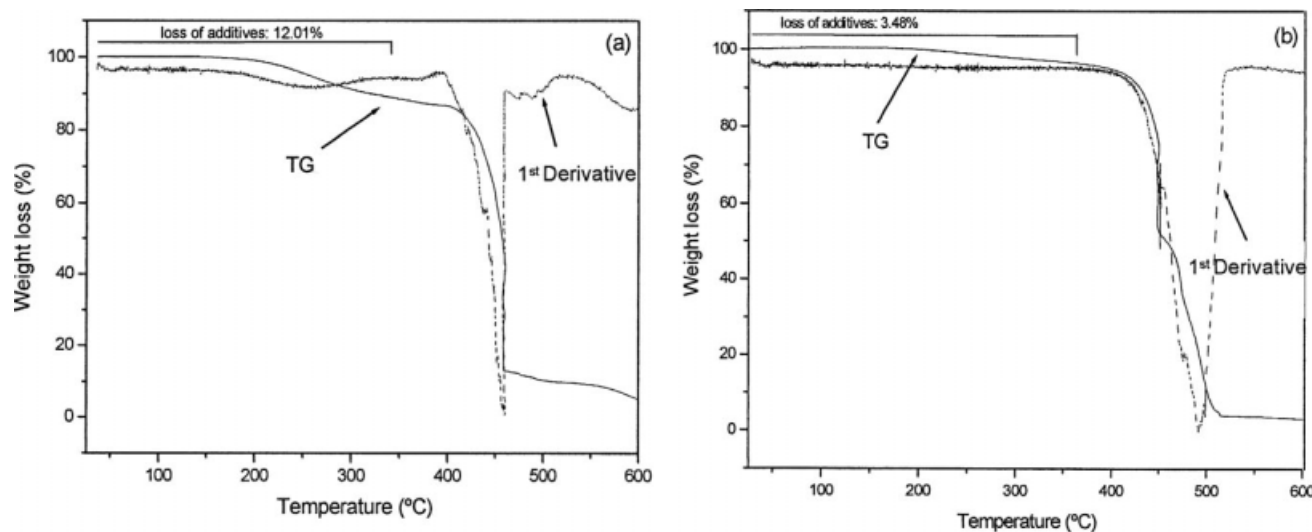


Figure 2 TG curves and their first derivative for (a) virgin and (b) PA-11 aged in deionized water for 9 days at 110°C.

Triplicate analyses agreed within 0.5%.¹³

$$IV = \frac{\ln(t/t_0)}{c} \quad (1)$$

The viscosity of the polymer solution can be affected by the presence of the plasticizer, as well as by other substances adsorbed on the sample. Therefore, it was necessary to measure the amount of substances of low molar mass present in the sample to calculate the corrected IV (CIV). The content of additives was determined by thermogravimetry and differential thermal analysis (TG/DTA) in a Shimadzu Thermal Analysis Apparatus, operating from 25 to 800°C, with a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The CIV was calculated with the corrected weight of polymer according to eq. (2), where the content of additives is expressed in weight percent.

$$CIV = [(IV)/(100 - \text{Additives})] \times 100 \quad (2)$$

The DSC experiments were performed in a Shimadzu DSC-50 calorimeter. Polymer samples of 5 mg were placed in crimped aluminum pans, with a hole for nitrogen circulation to prevent oxidative degradation. The heating and cooling rate was 10°C min⁻¹. In the first heating scans, the samples were heated from ambient temperature to 230°C. The crystallization process was recorded from 220 to 110°C. The second heating was performed from 110 to 260°C.

XRD measurements were conducted in a Rigaku diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), with 2θ ranging from 10° to 30°. The SEM experiments were performed using a JEOL Model JSM T-300 equipment, operating at 20 kV. The samples were gold-sputtered before the measurements. The determination of the chemical elements adsorbed on the surface of polymer aged in oilfield water was

studied in a JEOL JXA model 8900 RL apparatus, equipped with an EDS.

RESULTS AND DISCUSSION

Figure 2(a,b) shows the weight loss curves and first derivatives as a function of the temperature for virgin and PA-11 aged in deionized water for 9 days at 110°C. In Figure 2(a), the first derivative curve shows three weight loss processes. The first weight loss starts at 200°C and extends up to 350°C. This is due to release of volatile compounds, such as additives. The other two processes occur above 400 and 460°C and are not easily identified. In this region, there is a discrete maximum in the curve of the first derivative.²⁰ These two processes correspond to the decomposition of the polymer.²¹ In Figure 2(b), the first weight loss is less pronounced than that presented in the curve for virgin PA-11. This is due to a lower amount of additive in the aged PA-11 (3.48 wt %) than in virgin PA-11 (12 wt %). The other two decompositions are more evident in the curve obtained for the aged samples, occurring at intervals of temperature between 410 and 450°C and 450 and 515°C, respectively. The second decomposition step is more pronounced for aged PA-11, where the weight loss percentage increases from 40 to 50 wt % in this step.

The curves obtained for the loss of additives in the polymer matrix as a function of time are shown in Figure 3. These values were obtained from TG measurements. The initial loss of additives over time is faster at higher temperatures for both fluids. At 140°C in deionized water, the amount decreases to 2 wt % after 10 days. This is very different from what is seen in oilfield water at the same temperature. In both systems, the rapid loss of additives in both types of aqueous media is due to an increase in

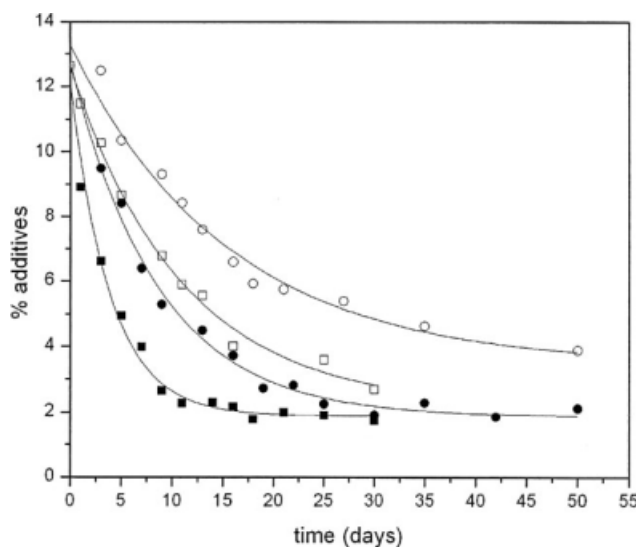


Figure 3 Percentage of additives in the polymer matrix vs. ageing time in deionized water (pH 7.0): (●) 120°C and (■) 140°C; and oilfield water (pH 5.5): (○) 120°C and (□) 140°C.

solubility of the additives as a function of temperature. Meanwhile, a substantially smaller loss of additives when PA-11 is aged in oilfield water can be attributed to the formation of a layer composed mainly of iron oxide on the surface of the polymer, hindering the leaching out of additives to the water. This interpretation is based on the results obtained from the EDS experiments discussed later.

The variation of the CIV with respect to ageing time is shown in Figure 4. The curves show that the CIV changes exponentially with time until a plateau is reached, where there is an equilibrium process.² The results show that the initial rate of decrease in viscosity is faster at higher temperatures. When comparing curves for the same temperature and different pH, there is a similar rate of CIV decrease indicating that the pH is not influencing the initial rate of degradation. After a certain time (almost 5 days for 140°C and 15 days for 120°C), the viscosity essentially has reached a constant value indicating that the degradation reaction has reached the equilibrium process. The viscosity plateau values for the oilfield water are lower than those observed in deionized water suggesting that the degradation process of the PA-11 is more severe at low pH. Therefore, the pH mainly affects the equilibrium process of the system. These results are in agreement with those reported by Merdas et al.,⁵ where two main acid effects on hydrolysis are reported: catalysis, of which the main consequence is an increase of hydrolysis rate, and amine scavenging with essentially, a shift of the equilibrium toward higher conversions, i.e., lower viscosities. To presume the effect of catalysis by H⁺ ions, the degradation kinetic (r) is given by eq. (3), where $[E]$ and

$[W]$ are amide and water ion concentrations in the polymer; $[AH]$ is the concentration of non dissociated acid; and k , k_W , and k_A are proportionality, water, and acid dissociation constant.

$$r = k k_W^{1/2} [E][W]^{3/2} (1 + y[AH])^{1/2} \quad (3)$$

where $y = k_A / (k_W [W])$.⁵

Catalytic effects are significant only if $y[AH]$ is of the order of unity or higher. In this work, weak organic acids are present in low concentration (pH > 5) and y is low [k_A of organic acids are low as in the case of chain end $(CH_2)_{10}COOH$ acids]. Therefore, the effect on hydrolysis rate is insignificant, in agreement with the experimental results where the pH has low or even negligible catalytic effects at low conversions (few days). Hence, at high conversions, i.e., close to equilibrium, another process, e.g., amine scavenging, can play an important role.⁵

The DSC curves of samples of virgin and aged PA-11 at 120°C in oilfield water are shown in Figure 5. The first heating cycle, Figure 5(a), shows a slight increase in the melting point (T_m) of the PA-11 with ageing time. The curve for the sample aged for 11 days shows a shoulder indicating a second T_m . This suggests the presence of compounds with lower molar mass in the polymeric matrix, like oligomers, which result from random chain scission reactions caused by product hydrolysis.^{3,6,22} This behavior is also commonly found in hydrolytic degradation studies of other linear polycondensates such as polyesters^{23,24} and polycarbonates.^{25,26} In Figure 5(b), a more pronounced increase in T_m can be observed for PA-11 as a function of ageing time. This is due to new, different sized crystallite formations that are dispersed and homogenized in the second heating

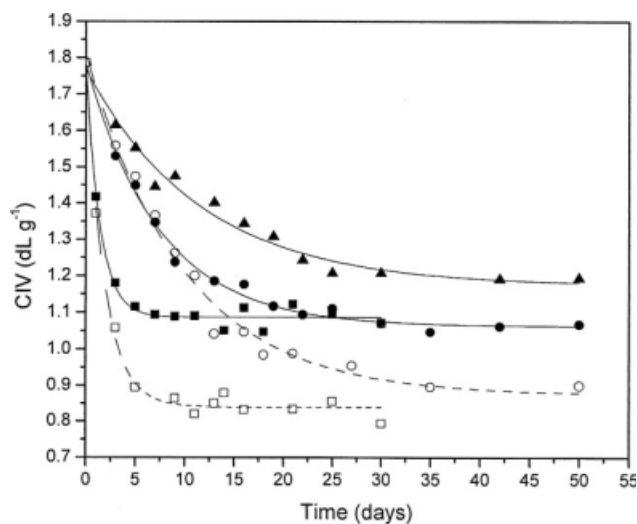


Figure 4 Change of corrected inherent viscosity against time in deionized water, pH 7: (▲) 110°C, (●) 120°C, and (■) 140°C; and in oilfield water, pH 5.5: (○) 120°C and (□) 140°C.

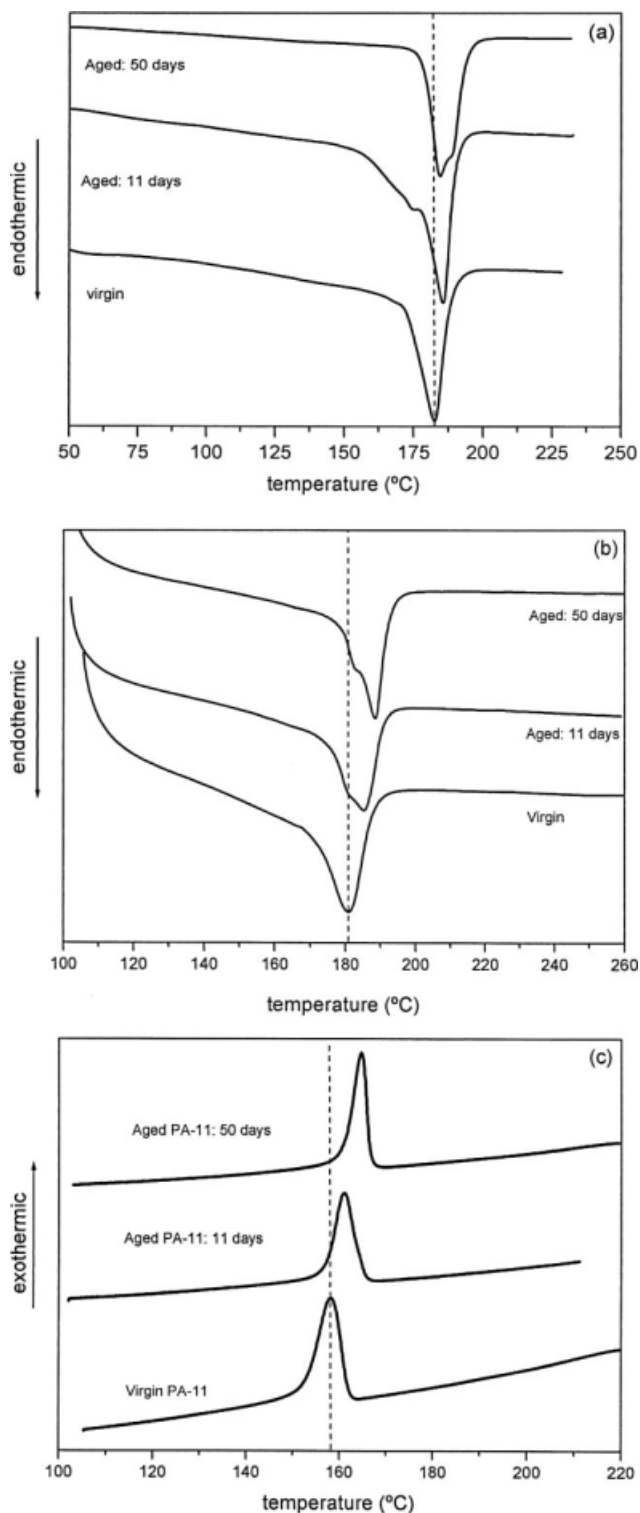


Figure 5 Virgin and PA-11 aged in oilfield water at 120°C: (a) first and (b) second DSC heating scans; and (c) DSC cooling scans.

cycle. The random chain scission process seems to improve chain packing and consequently shifts both the T_m and the crystallization temperature (T_c), Figure 5(c), to higher temperatures. Therefore, the hydrolytic degradation process also affects the

TABLE II
Thermal Characteristics of the Virgin and Aged PA-11

PA-11	T_c (°C)	T_m (°C) ^a	X_c (%) ^b
Virgin	158.1	181.7	28.97
Aged 11 days ^c	161.1	185.1	38.27
Aged 50 days ^c	164.7	187.9	33.02

^a Second heating scan.

^b Values obtained through XRD measurements.

^c Second heating scan in oilfield water at 120°C.

crystallization rate of PA-11 and the degree of crystallinity (X_c) increases as a function of ageing time. These data are summarized in Table II.

Figure 5(c) shows the first cooling of PA-11. An increase in T_c was also observed for the PA-11 samples aged for 11 and 50 days in oilfield water. These shifts are due to the increase in the amount of low molar mass compounds (oligomers) that give a higher mobility in the aged PA-11 chains. Consequently, when the PA-11 is cooling, a shift to higher values of T_c and the formation of a narrow crystallization peak was observed (50 days).

Figure 6(a–c) shows the XRD patterns of the virgin and PA-11 samples aged for 11 and 50 days in oilfield water at 120°C, respectively. It is known that PA-11 presents polymorphism with five crystalline phases.⁹ Figure 6(a) show two intense and broad reflectance (100) and (010, 110) at the diffraction angles 2θ of 20.22° and 23.07°, which are characteristic of the triclinic α -form. Therefore, the cell dimensions and angles associated to the reticulum give distinct values ($a = 0.49$ nm, $b = 0.54$ nm, and $c = 1.49$ nm, $\alpha = 49^\circ$, $\beta = 77^\circ$, $\gamma = 63^\circ$).^{20,27,28}

A new peak is observed in Figure 6(b) when the material is subjected to ageing at 120°C for 11 days. This peak indicates the appearance of a new

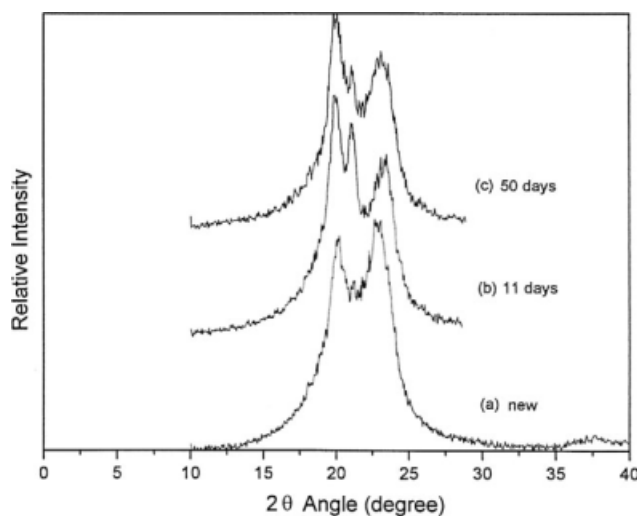


Figure 6 XRD pattern of (a) virgin and PA-11 aged in oilfield water at 120°C for (b) 11 days and (c) 50 days.

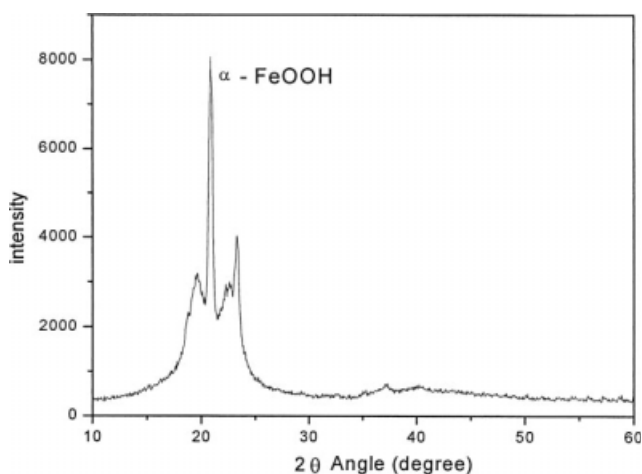


Figure 7 XRD of the residues from the PA-11 surface immersed in oilfield water.

pseudo-hexagonal γ -form with a diffraction angle 2θ of 21° . However, in the sample aged for 50 days [Fig. 6(c)] a decrease in the peak of this γ -form is observed, featuring a metastable behavior which is easily disturbed.²⁰ The disappearance of the γ -form peak associated with the process of hydrolytic degradation suggests that the process of degradation occurs preferentially in the amorphous region of the polymeric matrix.

Table II shows the X_c for the samples of virgin and aged PA-11 calculated from XRD measurements. The value of approximately 29% for virgin PA-11 is in good agreement with reported values.¹⁴ An increase in X_c is observed after 11 days of ageing in oilfield water at 120°C . Meanwhile, a lower X_c is observed after 50 days. This can be attributed to a smaller contribution of the pseudo-hexagonal form after 11 days.

The EDS measurements allowed the determination of the ions on the surface of PA-11 aged in oilfield water. The main atoms present on the polymer surface were calcium, aluminum, silicon, iron, copper, zinc, boron, phosphorus, sulphur, oxygen, and chlorine. The yellowish coloration of both the oilfield water and the polymeric surface may be associated to the high atomic percentage of iron and oxygen (together they correspond to 76%).

Iron oxides (a group name for iron oxyhydroxides and oxides) are widely dispersed in soils, sediments, rocks, and aquatic systems. They are produced from reactions of Fe^{3+} hydrolysis in aqueous media, where the nature of the anion present in the solution influences the hydrolysis of the Fe^{3+} ions.²⁹ These reactions are also involved in corrosion processes during the formation of rust (atmospheric or "wet" corrosion of steel).^{30,31} The XRD pattern of the residues from the polymeric surface, Figure 7, confirms

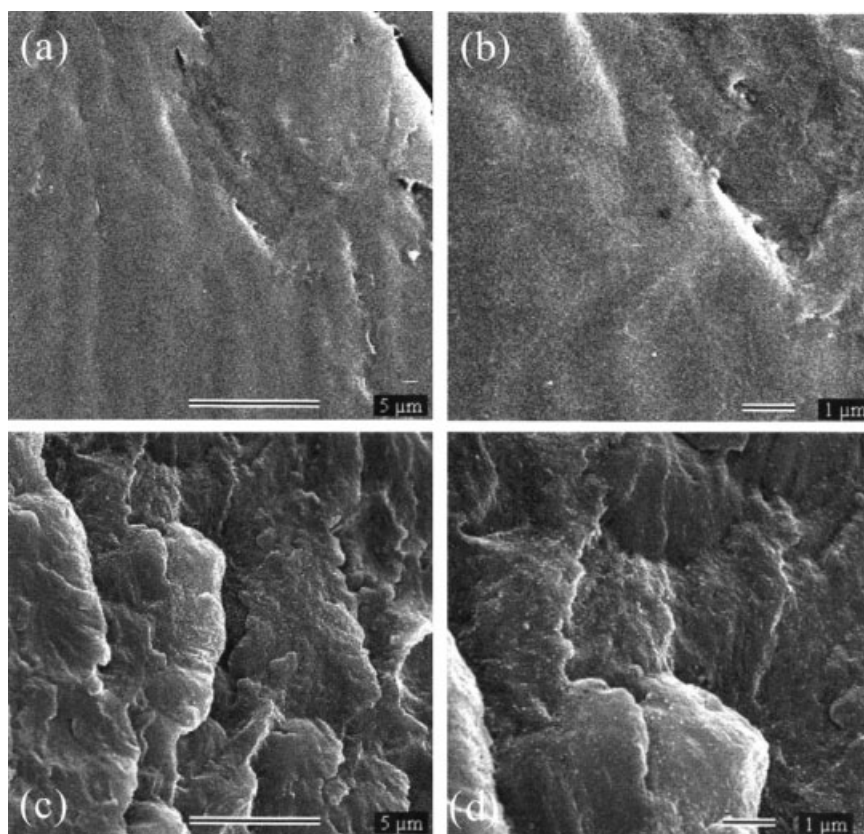


Figure 8 SEM micrographs of (a) and (b) virgin; (c) and (d) PA-11 aged at 120°C in oilfield water for 50 days.

the presence of iron hydroxides, α -FeOOH (goethite), evidenced by the intense peak at $2\theta = 20.87^\circ$ and in good agreement with reported values.³² Therefore, a lower extraction of the polymer additives by the oilfield water can be attributed to the formation of a protective layer composed mainly of Fe(III)-salts and oxides on the surface of the polymeric matrix, inhibiting the removal of the low molar mass additives and compounds by the aqueous media.

SEM images of the virgin and aged PA-11 are shown in Figure 8. The surface of the virgin PA-11 is smooth with no visible defects [Fig. 8(a,b)]. In contrast, the aged PA-11 subjected to 120°C in oilfield water for a period of 50 days had visible defects across its surface and evidence of future crack formation due to the increase in porosity [Fig. 8(c,d)]. Three mechanisms of crack formation in PA-11 are known,³ but only two are useful for the explanation of this morphologic formation. The first mechanism is an osmotic process that promotes the dissolution of organic compounds from the hydrolysis of the polymer in water. As a consequence, microcavities are observed on the surface of the polymer, which accelerate future crack propagation. The second mechanism is ascribed to the formation of pores and the propagation of cracks, when the material reaches a critical molar mass, M_c , corresponding to a CIV value $<1.0 \text{ dL g}^{-1}$. The material suffers a ductile/brittle transition, in accordance with the measurements of fracture toughness, and the mechanism becomes spontaneous.¹³ In this study, the CIV value of PA-11 aged for 50 days was 0.9 dL g^{-1} and no cracks were observed. Surface morphology changes are evidence for chemical attack caused by the oilfield water components associated with high temperature.

CONCLUSIONS

The results show that the hydrolytic degradation of the plasticized PA-11 used in oilfield pipes is accelerated by an increase in temperature and a decrease in pH. That compromises its durability over a short period of time when the temperature of operation is higher than 110°C. The results suggest that the initial rate of the hydrolysis process is mainly affected by temperature. When the system reaches equilibrium, the pH affects mainly the CIV plateau values. The formation of compounds with low molar mass, such as oligomers dispersed in the polymeric matrix, was indicated by the DSC measurements. The observed increase in crystallization and melting temperatures is due to the degradation process of random chain scission resulting from hydrolysis reactions. XRD measurements showed changes in the crystallinity of the PA-11 subjected to hydrolysis at high temperatures. These changes can be ascribed to preferential hydrolytic degradation at the amorphous domains of the

polymeric matrix, which leads to an increase in the crystallinity degree observed from XRD results. When the material suffers a ductile-brittle transition, $\text{CIV} < 1.0 \text{ dL g}^{-1}$, the formation of microcracks on the surface of the polymeric matrix was shown by SEM measurements. These contributed to accelerate the hardening of the material and the spreading of cracks.

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