Hydrolytic ageing of polyamide 11. 1. Hydrolysis kinetics in water

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Abstract

The hydrolysis mechanism of polyamide 11 for offshore applications has been investigated in detail. Very careful experimental procedures have been developed to avoid any overlaying oxidation reactions. During hydrolysis the main mechanism is chain scission of polyamide 11. The experimental results are well described by a kinetic model derived from the reaction of polyamide 11 with water. This model predicts the molecular weight evolution of polyamide 11 hydrolysis in pure water. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

The use of polymer materials in increasingly demanding applications requires a profound understanding of their durability and underlying ageing phenomena. This statement is particularly true for applications where polymer materials play a vital role in the security or safe functioning of an installation or a machine.

In offshore oilfield exploration, flexible pipe technology has gained importance as a convenient and effective way to connect seafloor wellheads to sea-level oil platforms. This application is a particularly challenging example for the use of thermoplastic polymers in demanding environments, the key function of the thermoplastic being the pressure containment of the produced fluids, mixtures of oil, gas and water [1]. Temperatures can be very high—well over 100 °C—and design lifetimes for such pipes can easily exceed 20 years.

Polyamide 11 was among the first polymers chosen for this application due to its outstanding flexural fatigue resistance, excellent creep resistance, high ageing resistance and high barrier properties in oil and natural gas. The special interest in the exact limits of the ageing performance of

polyamide 11 is thus justified but the desire exists to use the material up to its performance limits while preserving a maximum safety of the offshore pipeline installations [1].

Polyamide 11 is a semi-crystalline thermoplastic combining high tensile strength and creep resistance with a rather low modulus/high flexibility. Due to the high hydrocarbon proportion of the polymer repeat unit the typical water absorption characteristic of polyamide is greatly reduced compared to PA 6 or PA 6–6. Table 1 gives typical values for key properties of the plasticised and unplasticised polymer. In flexible pipes the plasticised variant is used because of the very high flexibility making it a rubber-like material. The plasticiser is benzene-butylsulfonamide and its nominal content is 12% per weight.

In general the ageing behaviour of thermoplastic polymers involves complex phenomena including changes in crystalline morphology, plasticiser and other low molecular weight molecules extraction, chain scission or crosslinking due to reaction with oxygen or other reactive species and/or mechanical damage such as voiding, shearing or creep. In the case of flexible pipes, polyamide 11 is exposed to an oxygen exempt environment. However, crude oil and natural gas contain species such as organic acids, water, carbon dioxide and hydrogen sulphide susceptible of chemical attack. Hydrocarbon aliphatic and aromatic molecules can be taken as inert apart from the lighter aromatic species which can be absorbed to some extent by polyamide 11.

In this paper we describe in detail the chain scission

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Table 1
Some properties of plasticised and unplasticised polyamide 11. Mechanical properties depend on moisture content. The standards cited integrate a precise conditioning procedure

Property	Method	PA 11, unplasticised	PA 11, plasticised
Melting point (°C)	ASTM D789	183–187	178–184
Density	ISO R 1183 D	1.03	1.05
Tensile yield stress (MPa)	ISO R 527	42	27
Flexural modulus	ISO 178	1000	350

induced by hydrolysis of polyamide 11. Among the different phenomena during ageing in oilfield service, hydrolysis has been identified as the prevalent chemical attack leading to a performance loss of the material.

A rational lifetime prediction model must therefore involve:

(i) A mechanistic scheme for hydrolysis. This scheme considers the polymer structure at the molecular scale (monomer unit). The key questions, at this level are:

The mechanism of acid effect. This problem will not be examined here, only the case of hydrolysis in neutral medium will be studied.

The existence or not of equilibrium in the conversion range of practical interest. When considering pure hydrolysis phenomenon, reversibility of polyamidification strongly supports the presence of an equilibrium process [2]. A temperature dependent polycondensation equilibrium has clearly been demonstrated for polyamide 12 in the molten state [3]. The question here is to extent this observation to polyamide 11 in the solid-state at lower temperatures.

(ii) A kinetic model derived from the mechanistic scheme. It must describe the time changes of amide concentration. The model parameters (rate constants, boundary conditions) must be explicit functions of the exposure variables: temperature, water activity, pH, etc. Is the reaction diffusion controlled or not?

(iii) A statistical model to convert amide consumption in terms of molar mass decrease. Here, eventual crystallinity effects (PA 11 crystallinity content is $\sim 25\%$ [4]) are neglected, it is considered that hydrolysis is a random chain scission process [5–7]. In a first approach, PA 11 can be considered as a common polycondensate having a polydispersity index close to 2. An interesting property of such polymers is that their polydispersity index remains always equal to 2 when they undergo a random chain scission [8].

(iv) A physical model establishing a link between molar mass and mechanical properties. In the case of amorphous or low crystallinity glassy polymers, embrittlement occurs suddenly as a result of destruction, by chain scission, of the entanglement network [9]. In a relatively sharp molar mass interval, the toughness, as represented, for instance, by the critical ratio of elastic energy release G_{1C}, varies of two or more orders of magnitude, which leads to the existence of a

ductile–brittle transition [10] at a critical molar mass M_F such as: $M_F = qM_c$ where M_c is the entanglement critical molar mass determined from rheological measurements and q is a factor such as $1 < q < 10$.

Since M_c is of the order of few kg mol^{-1} [11], M_F is generally of the order of 10 kg mol^{-1}.

In the case of polyamide 11, it has been effectively found that embrittlement occurs suddenly at a critical molar mass of the order of 10–20 kg mol^{-1} [1,12].

2. Experimental

The polyamide 11 under study is a plasticised extrusion grade Rilsan® BESNO P40 TL. Samples are ISO 527 1BA specimens (but with a 3 mm thickness) punched from extruded sheets.

In order to obtain sufficiently accurate experimental data to model polyamide 11 behaviour in field conditions, it is of primary importance to perform experimental tests in conditions as close as possible to the final use. Therefore, it is very important to avoid any other polyamide degradation process that could overlay hydrolysis degradation. The definition of a correct oxygen removal procedure is fundamental during any laboratory study devoted to polyamide ageing in field conditions.

The operating mode for oxygen removal in this study is precisely defined. Nitrogen comes from bottles (quality I or U—O$_2$ residual content is a few ppb). Bubbling is performed during at least 3 h in a 'closed' vessel. Nitrogen is conducted by a metallic tube to the bottom of the vessel and is removed by a small outlet with a closing valve. In these operating conditions, residual level of oxygen content at the exit of the vessel has been measured after 3 h as lower than 2 ppm. Vessels have a content of 1.5 l and can stand up to a pressure of more than 50 bars. Fluids are replaced at each sampling time in order for the closed system to model as best as possible the behaviour of an open system.

Demineralised water and/or normalised oil (gazole US2D/EPA94, ASTM D975-94 norm) are used as ageing environments.

Evaluation of polyamide 11 molecular weight degradation during hydrolysis has systematically been carried out by measuring solution inherent viscosity of aged specimens. Extractable content is measured on all samples and adequate
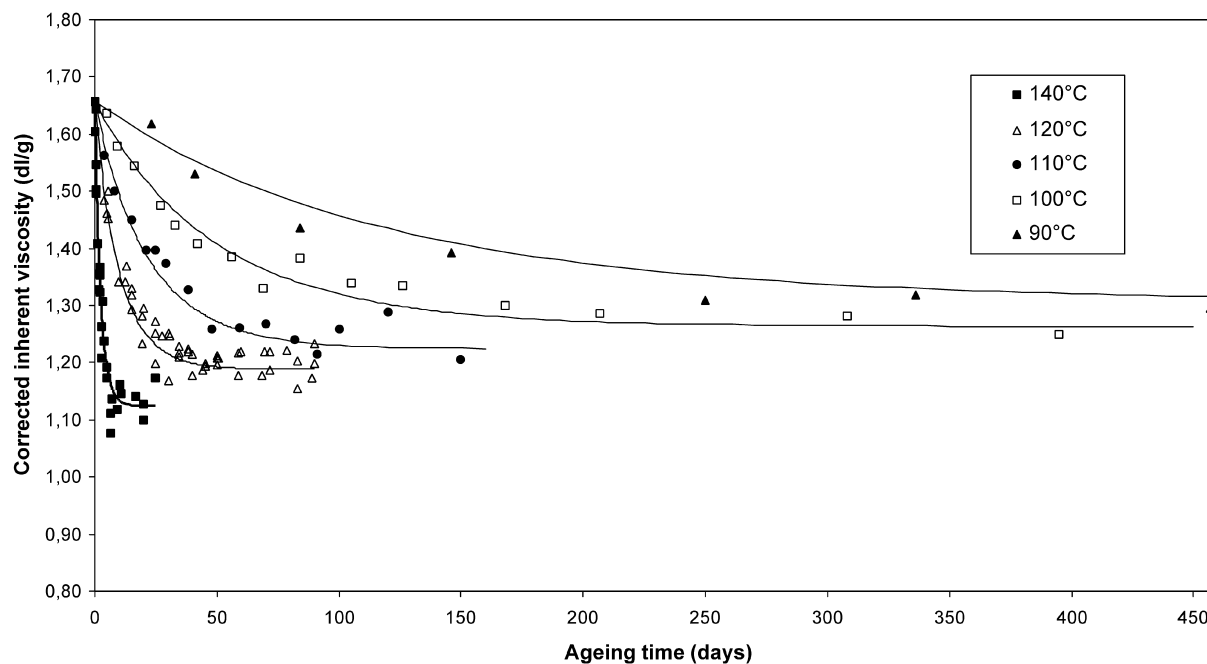
Fig. 1. Evolution of corrected inherent viscosity values of polyamide 11 samples aged in pure water at different temperatures. The fit curves have been generated following mathematical equations described below.

correction is realised for plasticiser concentration. The complete operating procedure has been specifically detailed and is completely described in an annex of a future API document [13].

Measurements of polyamide 11 molecular weight distributions and average values have also been carried out by size exclusion chromatography in benzyl alcohol at 130 °C [14].

Low molecular weight samples used to study hydrolytic ageing at 80 °C are additive-free laboratory made polyamide 11.

Water sorption experiments have been performed with 0.9 mm thickness polyamide 11 samples at different temperatures (23, 50, 75 and 100 °C) in distilled or salt water (30 g l^{-1}); samples have been weighted in the wet state.

3. Results and discussion

3.1. Results

Polyamide 11 ageing experiments carried out at 90, 100, 110, 120 and 140 °C in saturated, acid free water, in carefully deoxygenated reactors, lead to the inherent viscosity evolution shown in Fig. 1.

It clearly appears that the hydrolysis rate is temperature dependent. All inherent viscosity values go to a plateau value, supporting the existence of an equilibrium process. The exact level of the asymptotic 'plateau' value is slightly temperature dependent, increasing when ageing temperature

decreases, in good agreement with data for polyamide 12 in the molten phase [3].

Evolution of polyamide samples during ageing has also been studied by size exclusion chromatography measurements. Exactly identical evolution could be depicted using average-molecular weight values instead of inherent viscosity measurements. No significant polydispersity change has been observed on aged specimens. Correspondence between measured values can be expressed by a 'Mark-Houwink type' relationship between weight-average molecular weight and corrected inherent viscosity, as depicted in Fig. 2.

A specific experiment has been carried out with low molecular weight polyamide 11 samples, aged in pure deoxygenated water at 80 °C, in order to see the beginning of molecular weight evolution at lower temperature. Results are presented in Table 2. These data show a molecular weight increase, indicating a predominance of polycondensation over hydrolysis for these samples, at the temperature under study.

Some ageing experiments have been carried out with mixtures of water and normalised oil, in order to compare polyamide molecular weight evolution depending on water content in the ageing fluid. Similar results have been obtained with viscosity or SEC evaluation of aged samples. Fig. 3 shows the evolution of polyamide 11 samples aged at 140 °C in different water/oil mixtures. It is observed that 1 or 5% of water in oil induces similar polyamide molecular weight decrease as pure water. On the opposite, with an oil totally free of water, a very important molecular weight increase is observed.
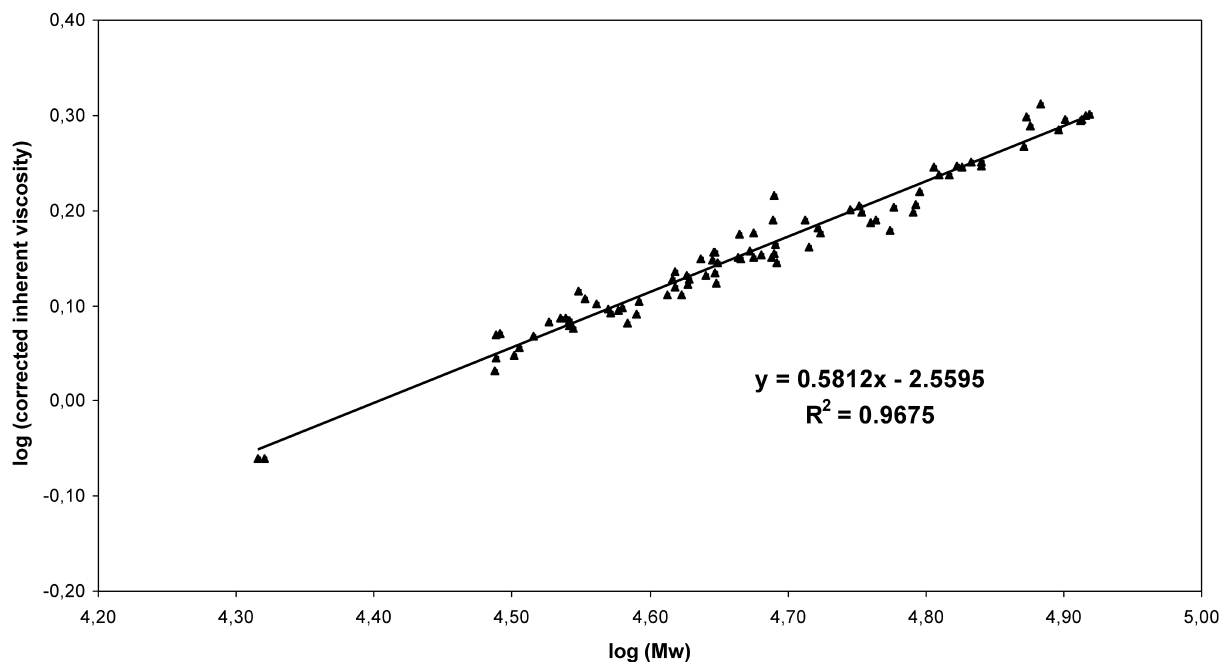
Fig. 2. Correspondence between measurements carried out on polyamide 11 samples, at different levels of hydrolysis ageing, between corrected inherent viscosity values and weight-average molecular weight values, obtained from SEC measurements.

3.2. Theory

3.2.1. Basic equations

In the most general case, hydrolysis is an equilibrated process:

$$\text{amide} + \text{water} \underset{k_R}{\overset{k_H}{\rightleftharpoons}} \text{acid} + \text{amine}$$
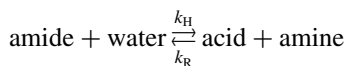
If E, W, A and B represent, respectively, the amide, water, acid and amine concentration and n the number of chain scissions (expressed in mol kg^{-1}) at time t, it can be written as

$$n = \frac{1}{M_n} - \frac{1}{M_{n_0}} \tag{1}$$

and

$$n = E_0 - E = A - A_0 = B - B_0 \tag{2}$$

where M_n is the number-average molar mass and the subscript zero corresponds to the initial (virgin) state.

The basic kinetic equation can thus be written as:

$$r = \frac{dn}{dt} = k_H EW - k_R AB$$

$$= k_H (E_0 - n)W - k_R (A_0 + n)(B_0 + n) \tag{3}$$

In a general case, water distribution in the polymer is not homogeneous so that it is necessary to take into account its diffusion and consumption rates. The latter is equal to the chain scission rate:

$$r(W) = \frac{dW}{dt} = k_H EW - k_R AB \tag{4}$$

Thus, the local change of water concentration at a depth x in the sample thickness is given by

$$\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2} - r(W) \tag{5}$$

where D is the diffusion coefficient of water in PA 11.

Using the set of Eqs. (1)–(5), it is possible to determine at each time and each depth layer the water concentration, W

Table 2
SEC average molecular weights measured on low molecular weight polyamide 11 samples, after ageing at 80 °C in carefully deoxygenated water

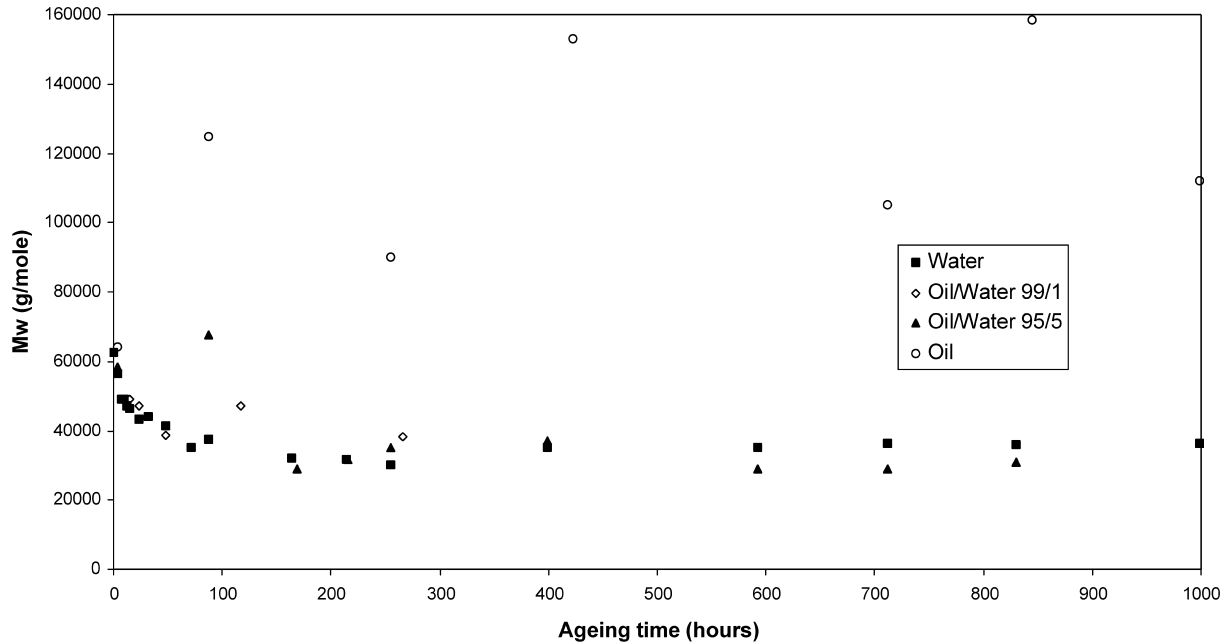| Experiment	Initial values			After 200 days at 80 °C		
	M_{w0} (kg mol^{-1})	M_{n0} (kg mol^{-1})	I_p	M_w (kg mol^{-1})	M_n (kg mol^{-1})	I_p
Sample A	6.6	3.4	1.9	10.2	5.5	1.9
Sample B	15.4	8.0	1.9	19.1	10.8	1.8
Sample C	22.3	12.3	1.8	26.5	13.4	2.0

Fig. 3. Weight-average molecular weight (determined by SEC) evolution of polyamide 11 samples aged at 140 °C in different carefully deoxygenated mixtures of demineralised water and normalised oil: (100/0; 5/95; 1/99; 0/100). Percentages are expressed as wt%.

and then the hydrolysis rate $r(W)$. By integration of this latter, the number of chain scissions per mass unit in each layer is obtained:

$$n(x) = \int_0^t r_x \, dt \tag{6}$$

We will consider some simplified kinetic schemes:

It has been experimentally shown [12] that an important decrease of mechanical properties occurs at a critical molar mass M_{nF} of the order of magnitude of 15 kg mol^{-1}. For the polyamide 11 sample under study ($M_{n0} \sim 30$ kg mol^{-1}), the number of chain scissions per mass unit necessary to reach this critical molar mass should thus be:

$$n = \frac{1}{M_{nF}} - \frac{1}{M_{n0}} \approx \frac{1}{30} \text{ mol kg}^{-1} \tag{7}$$

On the other hand, the total number of amide groups is initially

$$E_0 = \frac{1}{m} = 5.46 \text{ mol kg}^{-1} \tag{8}$$

where m is the molar mass of the monomer unit (0.183 kg mol^{-1}).

The conversion ratio at the critical molar mass is thus:

$$x_F \sim n_F/E_0 \sim 5 \times 10^{-3} \tag{9}$$

In other words, in the conversion range of interest, n can be neglected relatively to E_0.

A second simplification arises from the fact that, according to the polymerisation process, amine and acid chain ends must be in almost stoichiometric ratio:

$$A_0 = B_0 \tag{10}$$

With these two hypotheses, kinetic equation (3) becomes

$$\frac{dn}{dt} = k_H E_0 W - k_R (A_0 + n)^2 \tag{11}$$

where W is the water concentration in the *polymer*. In a thin superficial layer, $W = W_p$, depends on temperature and water activity in the surrounding medium, and is only determined by a polymer/medium physical equilibrium. In the case under study, where water is mixed to oil, two important quantities are to be considered: the actual water concentration in oil (C) and the saturation level of this concentration (C_s) (for $C > C_s$, water and oil form a diphasic system). If W_s is the water concentration in PA 11 immersed in oil saturated by water, one can write:

$$\frac{W_p}{W_s} = \frac{C}{C_s} \qquad \text{for } C \leq C_s$$

$$\tag{12}$$

and $W_p = W_s \qquad \text{for } C \geq C_s$

Eq. (12) expresses that the equilibrium of the water concentrations in the polymer and the liquid medium arises from the equality of chemical potentials. It should be noticed that, due to the low hydrophilicity of oil, low values of water concentration in oil (C) can reach saturation level (C_s).

For a given medium composition, e.g. for a given value of W_p, there are two important cases depending on water diffusion limits or not the hydrolysis rate.

3.2.2. Case 1. Non-diffusion controlled kinetics

In this case, water diffusion does not limit the hydrolysis rate. Water is in excess in the whole sample volume, $W = W_p$ in all sample layers, hydrolysis is homogeneous, the

course of degradation is described by Eq. (11) of which the integration leads to

$$M_n = M_{ne} \frac{M_{n0}^{-1} + M_{ne}^{-1} + (M_{ne}^{-1} - M_{n0}^{-1})\exp(-Kt)}{M_{n0}^{-1} + M_{ne}^{-1} - (M_{ne}^{-1} - M_{n0}^{-1})\exp(-Kt)} \quad (13)$$

where M_{ne} is the asymptotic (equilibrium) molar mass given by

$$M_{ne} = \left(\frac{k_R}{k_H E_0 W_p}\right)^{1/2} \quad (14)$$

and K (pseudo first order rate constant) is given by:

$$K = 2(k_R k_H E_0 W_p)^{1/2} = 2\, k_R M_{ne}^{-1} \quad (15)$$

Experiments lead to the determination of K and M_{ne} (see below), from which it is possible to determine the basic rate constants k_R and k_H:

$$k_R = \frac{K M_{ne}}{2} \text{ and } k_H = \frac{K}{2 M_{ne} E_0 W_p} \quad (16)$$

In the case of a saturated medium ($W_p = W_s$), W_s is supposed to obey an Arrhenius law

$$W_s = W_{s0} \exp - \frac{E_W}{RT} \quad (17)$$

with $E_W \sim 4\,\text{kJ mol}^{-1}$ [15], and $W_s \sim 1\,\text{mol kg}^{-1}$ in the temperature domain under study.

Thus, according to Eq. (14), M_{ne} must also obey Arrhenius law, with an apparent activation energy

$$E_{M_{ne}} = \tfrac{1}{2}(E_R - E_H - E_W) \quad (18)$$

where E_R and E_H are the respective activation energies of k_R and k_H.

In the same way, the apparent activation energy of K would be, according to Eq. (15)

$$E_K = \tfrac{1}{2}(E_R + E_H + E_W) \quad (19)$$

K is therefore expected to be considerably more sensitive to temperature variations than M_{ne}.

Eqs. (14) and (15) allow also to predict the effect of water concentration (e.g. water activity in the liquid medium) on the kinetic characteristics: K increases proportionally to $W_p^{1/2}$, whereas M_{ne} increases proportionally to $W_p^{-1/2}$. In other words, an increase in water concentration leads to faster (K increases) and 'deeper' (M_{ne} decreases) hydrolysis.

It is noteworthy that there is a value of W_p (water activity in the liquid medium) for which the equilibrium molar mass M_{ne} is equal to the initial molar mass M_{n0}.

If $M_{n0} > M_{ne}$, then hydrolysis predominates and molar mass decreases with time.
If, in contrast, $M_{n0} < M_{ne}$, then polycondensation predominates and molar mass increases.

For a given polymer of initial molar mass M_{n0}, the critical water concentration W_{p0} is given by Eq. (20):

$$W_{p0} = \frac{k_R}{k_H} \frac{1}{E_0 M_{n0}^2} \quad (20)$$

3.2.3. Case 2. Diffusion controlled kinetics

In this case, water diffusion limits the hydrolysis rate, water concentration is a decreasing function of the sample depth layer. Then, the kinetic model needs a coupling of hydrolysis kinetics with the diffusion kinetic equation.

Starting from Eqs. (4), (5) and (11), it can be written as

$$\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial x^2} - (aW - b) \quad (21)$$

where $a = k_H E_0$ and $b = k_R(A_0 + n)^2$.

It is convenient, here, to take the origin of x-axis in the middle of the sample thickness so that the coordinates of the surfaces are $x_1 = +(L/2)$ and $x_2 = -(L/2)$, L being sample thickness. The boundary condition is $W = W_p$ at $x = +(L/2)$ and $x = -(L/2)$.

The integration of Eq. (21) leads to

$$W = \frac{b}{a} + \left(W_p - \frac{b}{a}\right)\frac{\text{ch}(x/x_0)}{\text{ch}(L/2x_0)} \quad (22)$$

where

$$x_0 = (D/a)^{1/2} \quad (23)$$

The thickness profile of water concentration will thus be symmetrical, with a minimum in the middle of the sample.

It can be noticed that b/a ratio decreases with time and tends towards W_p at equilibrium. This means that the initially heterogeneous system tends to homogenise as hydrolysis conversion approaches equilibrium.

Influence of sample thickness can be easily deduced from Eq. (22):

If L/x_0 is small, the initial degree of heterogeneity (water concentration gradient) is low. For instance, for $L \leq x_0$, concentration W_M in the middle of sample thickness is such as $W_M \geq 0.89\, W_p$. In other words, for $L \leq x_0$, hydrolysis can be considered as almost homogeneous.
If L/x_0 is high, hydrolysis is diffusion controlled; water distribution within sample thickness is non-uniform, sample skin layer is more degraded than core. In this case, degradation heterogeneity induces large problems if sampling for molecular mass determination is performed through whole thickness.

It appears thus important to determine experimentally D (from sorption experiments), and $a = k_H E_0$ (from hydrolysis experiments on thin films to be sure that reaction is not diffusion controlled), and to compare the thickness L to $x_0 = (D/a)^{1/2}$ in order to determine the kinetic regime of hydrolysis.

3.2.4. Practical use of the model

It is convenient to use molar mass ratios in order to minimise systematic errors.

Thus, taking $\lambda = M_n/M_{n0}$ and $\lambda_e = M_{ne}/M_{n0}$, one can linearise Eq. (13) as follows

$$y = y_0 + Kt \tag{24}$$

where

$$y = \ln \frac{\lambda + \lambda_e}{\lambda - \lambda_e} \text{ and } y_0 = \ln \frac{1 + \lambda_e}{1 - \lambda_e} \tag{25}$$

A major reason preventing to get correct values of λ could be the presence of residual oxidation due to incomplete/ inadequate purge of the reactor vessel. Such reactions overlay the hydrolysis reaction, creating a supplementary source of chain scission mechanism.

The preferred procedure to reduce the source of discrepancy is the use of an optimisation iterative method to search λ_e and K values giving the best linear correlation between y and t.

The kinetic model will be considered valid only if the correlation coefficient of the linear regression (R^2) is sufficiently high, for instance, $R^2 > 0.9$.

4. Discussion

The treatment of our experimental results according to Eqs. (24) and (25) leads to data presented in Table 3 and the fitting curves in Fig. 1.

These results call for the following comments.

Despite a noticeable data scatter in certain cases (especially at 120 °C), it can be reasonably considered that the results are in good agreement with the model of equilibrated hydrolysis. There is, no doubt, an equilibrium corresponding to a M_{ne} value of 18 ± 3 kg mol^{-1}. The fact that this equilibrium was not found in other studies [16,17], can be attributed to the presence of acids in water (or oxygen inducing acid creation).

The pseudo first order constant K varies with temperature and this dependence is reasonably well described by an

Arrhenius law (correlation coefficient R^2 is 0.99)

$$K = K_0 \exp\left(-\frac{E_K}{RT}\right) \tag{26}$$

with $K_0 = 7 \times 10^{11}$ days^{-1} and $E_K = 97$ kJ mol^{-1}

As expected, the asymptotic value of M_{ne} is less influenced by temperature. However, a rigorous statistical treatment of our results indicate a significant effect of λ_e decrease with temperature. This dependence obeys, apparently, Arrhenius law

$$M_{ne} = M_{ne0} \exp\left(-\frac{E_M}{RT}\right) \tag{27}$$

with $M_{ne}0 = 2.36$ kg mol^{-1} and $E_M/R = -777$ K.

This exact expression of this dependence is to be considered cautiously owing to the small variation of M_{ne} and the difficulty to appreciate the incertitude on λ_e determination with the chosen optimisation procedure.

From the above results, it is possible to determine the basic hydrolysis (k_H) and polycondensation (k_R) constants using Eq. (16) (Table 4). Polycondensation is therefore intrinsically more than 1000 times faster than hydrolysis in the temperature domain under study and the ratio is expected to increase as temperature decreases below 90 °C.

In a first approach, it was hypothesised that hydrolysis should be non-diffusion controlled because SEC measurements revealed no significant polydispersity increase. Nevertheless, this has been checked by a rigorous approach. Results of sorption experiments have led to the following expression (Eq. (28)) of water diffusion

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{28}$$

with $D_0 = 0.0132$ m^2 s^{-1} and $E_D/R = 7413$ K

It is therefore possible to calculate the data of Table 5.

It appears that x_0 is always far higher that the sample thickness used in this study and increases when temperature decreases. Degradation gradients due to the diffusion control of hydrolysis kinetics can be neglected and Eqs. (13)–(20) can be considered valid in the whole domain of conditions under consideration. This will be not necessarily true in the presence of acids if the reaction rate (k_H) is

Table 3

Mathematical treatment of hydrolysis data obtained for different polyamide 11 hydrolysis experiments carried out at various temperatures

Temperature (°C)	λ_e	K (day^{-1})	y_0	R^2
140	0.50	0.401	1.11	0.95
120	0.57	0.089	1.31	0.83
110	0.60	0.038	1.37	0.98
100	0.64	0.016	1.51	0.98
90	0.65	0.0090	1.55	0.95

Table 4

Hydrolysis and polycondensation basic constants, determined from different polyamide 11 hydrolysis experiments carried out at various temperatures

Temperature (°C)	M_{ne} (kg mol^{-1})	k_R (kg mol^{-1} day^{-1})	k_H (kg mol^{-1} day^{-1})	k_R/k_H
140	15.2	3.05	24.1×10^{-4}	1268
120	17.4	0.77	4.7×10^{-4}	1649
110	18.0	0.34	1.9×10^{-4}	1774
100	19.3	0.15	0.75×10^{-4}	2028
90	19.6	0.09	0.42×10^{-4}	2107

Table 5
Determination of the 'critical' thickness x_0 for diffusion control

Temperature (°C)	$a = k_H E_0$ (s^{-1})	D (m^2 s^{-1})	$x_0 = (D/a)^{1/2}$ (cm)
140	152×10^{-9}	21.29×10^{-11}	3.7
120	30×10^{-9}	8.55×10^{-11}	5.4
110	12×10^{-9}	5.22×10^{-11}	6.6
100	5×10^{-9}	3.11×10^{-11}	8.1
90	3×10^{-9}	1.80×10^{-11}	8.2

increased and the diffusion of acid species is lower than for water.

In order to completely evidence by an opposite way the reality of an equilibrium process generating the observed plateau in molecular weight values, it seemed interesting to study the hydrolytic ageing of samples having a molar mass lower than the equilibrium value M_{ne}. It was chosen to work at 80 °C in order to have supplementary information on the behaviour at low temperatures. The results are summarised in Table 6 and call for the following comments:

(i)   The molar mass increases, as expected from the model. This indicates that at least a part of amine–acid condensation reactions result effectively from random encounters of amine and acid chain ends, as postulated by the model.
(ii) In the case where $M_{n0} < M_{ne}$, the rate constant K can be determined from the following relationship

$$K = \frac{1}{t}\,\ln\left[\left(\frac{\lambda_e - 1}{\lambda_e + 1}\right)\left(\frac{\lambda + \lambda_e}{\lambda_e - \lambda}\right)\right] \qquad (29)$$

To evaluate K, it was assumed that $M_{ne} \sim 20\ \text{kg mol}^{-1}$ at 80 °C as estimated from the trend observed in Table 4. Values of K are presented in Table 6. They range between 0.9×10^{-3} and 1.7×10^{-3} days^{-1}, whereas extrapolation of Arrhenius equation (16) would give $K \sim 3.6 \times 10^{-3}$ days^{-1}.

Taking into account the various sources of incertitude (determination of K from a single point, M_{ne} obtained from a rough estimation), it can be considered that both theoretical and experimental K values are in acceptable agreement and that PA 11 hydrolysis is well represented by the chosen model, at least in the 80–140 °C temperature range.

The similarity of polyamide 11 molecular weight decrease in hydrolysis experiments carried out in oil/water

Table 6
SEC average molecular weights measured on low molecular weight polyamide 11 samples, after ageing at 80 °C in carefully deoxygenated water, and rate constant K deduced therefrom

Experiment	M_{n0} (kg mol^{-1})	M_n (kg mol^{-1})	$K \times 10^3$ (day^{-1})
Sample A	3.4	5.5	1.1
Sample B	8.0	10.8	1.8
Sample C	12.3	13.4	0.9

mixtures compared to pure water, as presented in Fig. 3, exemplifies the low value of the water saturation level C_s in the considered oil. 5%, or even 1% water added to the normalised oil are enough to reach this saturation level. Therefore, polyamide hydrolysis process occurs as in pure water, as predicted by the theoretical development.

On the opposite, due to the very low hydrophilic character of the normalised oil, experiments carried out in pure oil can be considered as nearly free of any water. The observed important polyamide molecular weight increase during ageing experiments (in the absence of oxidation processes) well reflects the presence of an equilibrium process displaced to polycondensation process due to the quasi-complete absence of water in the ageing medium. The important scattering of results during ageing time—with molecular weight levels always higher than the initial value—can also be explained by the very low residual water amount present in the ageing vessels. A limited variation of water traces between different samplings is enough to cause differences on reached equilibrium levels, and therefore to explain the observed scattered values.

5. Conclusions

The evolution of polyamide 11 ageing by an exclusive hydrolysis mechanism has been investigated. The experimental difficulty has been to avoid any overlaying oxidation reactions. It can be shown that carefully conducted experiments agree well with a kinetics model rigorously derived from the reaction of polyamide with water. The presence of an hydrolysis/polycondensation equilibrium has been evidenced for polyamide in the solid-state at least in a 90–140 °C temperature range. It has also been emphasised that the range of temperatures and polyamide thickness used for offshore applications and for our laboratory experiments is completely adequate for a non-diffusion controlled kinetics scheme of hydrolysis in pure water. A full kinetics model is now available to predict molecular weight evolution of polyamide 11 hydrolysis in pure water. In order to adequately model real ageing conditions in offshore oilfield exploitation, effects of acids will be studied in another paper. The correspondence between molecular weight decrease and mechanical evolution will also be detailed elsewhere.

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