Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions

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Abstract:

Polymers are widely used for passive thermal insulation coatings on steel pipe in offshore oil and gas production. In this industry, structures used in deep sea have to be reliable, as they are in service for more than 20 years in a very severe environment: sea water, hydrostatic pressure and temperature gradient. One of the main questions is how to test and predict the lifetime of such structures in the laboratory? This study presents one approach that has been developed to characterize and predict the degradation of polymers used as thermal insulation materials.

This paper is dedicated to polyurethane (polyether based) degradation in sea water at high temperature. Ageing has been performed in natural sea water under hydrostatic pressure at temperatures ranging from 70 to 120 °C on 2 mm thick samples. Water diffusion in the material and hydrolysis have been characterized using mass evolution and tensile tests. Based on these results, a model for the urethane hydrolysis reaction is proposed.

Keywords : Polyurethane ; Hydrolysis ; Accelerated ageing ; Sea water ; Coating ; Offshore

1. Introduction

When considering oil extraction in offshore conditions, one of the most important issues is flow insurance, i.e. the ability to transport extracted oil from the bottom of sea to production plant situated on surface. To ensure

this transport and avoid hydrate formation, the temperature of the fluid, which could be up to 100°C (depending on field characteristics) when extracted, has to be kept above 40°C inside the steel pipes while the external sea water is at 4°C. Thus in order to avoid overcooling of the oil, thick external passive thermal insulation layer is used as coating on pipes. Because of their good thermal properties, polymers are widely used for this insulation application; the most widely used materials are currently Polyurethane (PU) and Polypropylene (PP), with a thickness between 50 and 80 mm. However, one issue for this application is the ageing of the polymer material with respect to the reliability of the insulation layer over many years [1] [2] [3]. In fact, structures used in the offshore oil industry need, at least, a 20 year life time in service with a minimum of maintenance, in spite of a very severe environment, i.e. sea water, temperature, hydrostatic pressure, mechanical loading. It is thus necessary to evaluate long term behaviour of such structures using accelerated ageing tests in the laboratory so an important question is how to test and predict durability of polymers in such an environment. This study will focus on testing, characterization and life time prediction of a polyurethane used as thermal insulation layer and especially on accelerated ageing of the material itself in order to set up a degradation model.

Polyurethane polymers are widely used in a marine environment and present good long term behaviour when well formulated. In fact, PU based on polyester undergoes fast hydrolysis even at low temperature in water [4] [5] [6] [7] and so cannot be used for long term sea water applications. However, when PU is based on polyether it shows good behaviour in sea water at low temperature and can be used for long durations [8] [9] [10] [11]. Nevertheless under very severe conditions the urethane linkage can undergoes hydrolysis. The chemical reactions involved in this degradation have been identified under both acidic and basic conditions [12] [13] [14]. All these authors found that in polyether based PU, the most labile bond is the urethane one. Chemicals reactions during hydrolysis can be written as in figure 1 [14][15][16][17]:

This degradation leads to a decrease of network density in the polymer and to significant modifications to the mechanical properties of the elastomer [17].

This paper will describe accelerated ageing of a commercial PU in sea water at temperatures up to 120°C for periods up to 18 months with an evaluation of water diffusion in the material and changes in mechanical properties.
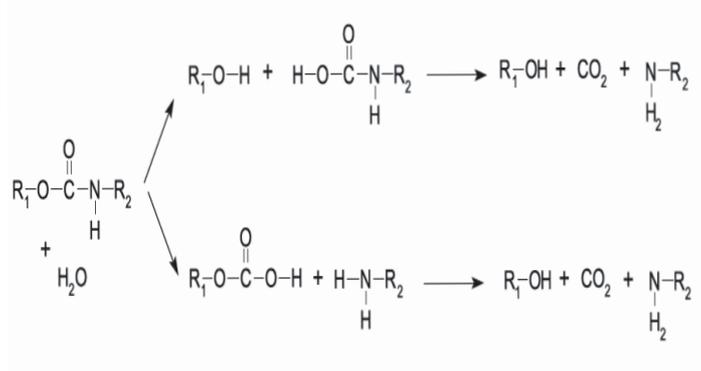
Figure 1: Chemical reactions involved in urethane hydrolysis

2. Experimental details

2.1. Material

The sample studied here is a commercial polyether-based polyurethane widely used for passive thermal insulation. This PU is made by reacting polyether polyol with MDI using 1,4-Butanediol as chain extender.

2.2. Accelerated ageing

Ageing was performed in natural renewed sea water at different temperatures from 25°C to 120°C for up to 18 months. Sea water came directly from Brest estuary and is renewed every day to avoid any contamination by degradation products. For temperatures above 95°C, ageing was performed under hydrostatic pressure (100bars).

2.3. Weight change

The water diffusion was determined from the weight evolution of square samples (50mm*50mm) with two different thicknesses (2 and 4 mm). Mass gain was followed by periodic weighing on a Sartorius LA 310 S balance (precision 0.1 mg). Samples were removed from the ageing containers and wiped with paper towels before weighing to dry the surfaces. The mass change (M) of each sample at time t is expressed as a percentage as :

$$M(t) = \frac{m(t) - mo}{mo}.100 \qquad (1)$$

Where m(t) is sample mass at time t and mo is the initial sample mass before immersion. For each condition (temperature, pressure and thickness), 3 samples were weighed to ensure the reliability of the measurement. The value of the water diffusion coefficient is calculated as the slope of the normalized mass evolution as a function of square root of time divided by sample thickness.

2.4. Tensile tests

Prior to ageing 2mm thick samples were cut from the sheets with a punch die in order to obtain normalized dumbbell shapes (type 2 from the standard ISO 37 [18]). After ageing, samples were store for 24h in sea water at room temperature before testing, i.e. samples were tested in the wet condition. For each condition, 3 samples were tested using an Instron machine with a 500 N load cell at 500 mm/min.

3. Results

3.1. Water Diffusion

Figure 2 shows mass change as a function of square root of time normalized by sample thickness when PU samples are immersed in sea water at 80°C.
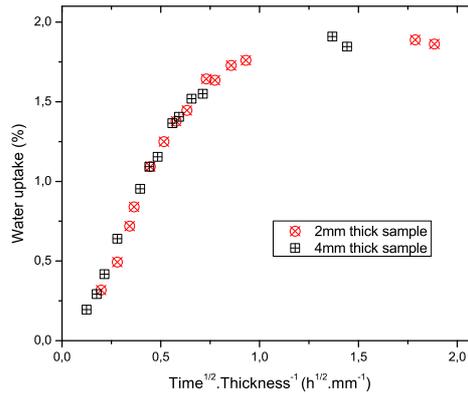

Figure 2: Water uptake in PU when immersed at 80°C in sea water

A typical Fickian behavior is observed in figure 2, in fact at the beginning of immersion water up take is directly proportional to the square root of time

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normalized by sample thickness and then, for longer durations, a plateau is reached [19][20][21]. Utilization of two different sample thicknesses is very useful to check that water absorption follows a Fickian behavior.

It is thus possible to model water absorption in this PU using the following equation:

$$\frac{dC}{dt} = D.\frac{d^2C}{dx^2} \tag{2}$$

Where C is water concentration (mol/L), D is water diffusion coefficient (m^2/s), t is time (s) and x the position in the sample (m).
A temperature effect on water absorption in PU can be observed in figure 3. Maximum water up take is constant for all ageing temperatures meaning that water solubility does not evolve with temperature. At the same time it is obvious that temperature affects water diffusion kinetics: an increase in temperature leads to faster water diffusion.
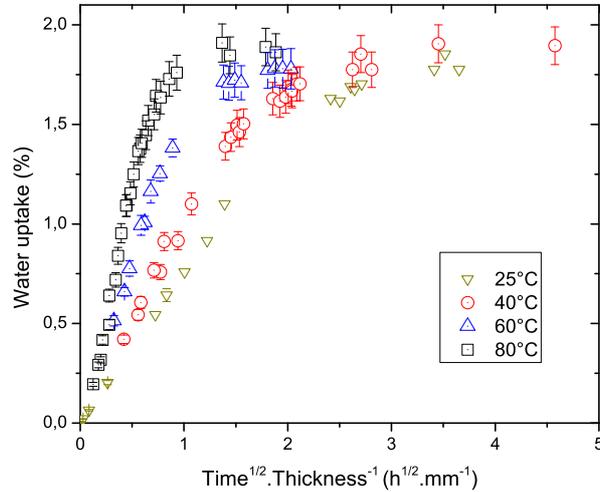

Figure 3: Temperature effect of sea water diffusion in PU

This temperature dependence is plotted in figure 4, it appears that the temperature effect on the kinetics of water diffusion into the polymer can be

fitted using the following Arrhenius law :

$$D = Do.\exp\frac{-Ea}{RT} \qquad (3)$$

Where D is water diffusion coefficient (m²/s), Do is pre-exponential factor (m²/s), Ea is activation energy (J/mol), R is the perfect gaz constant (m² .Kg/(s² .K.mol)) and T is temperature (K).
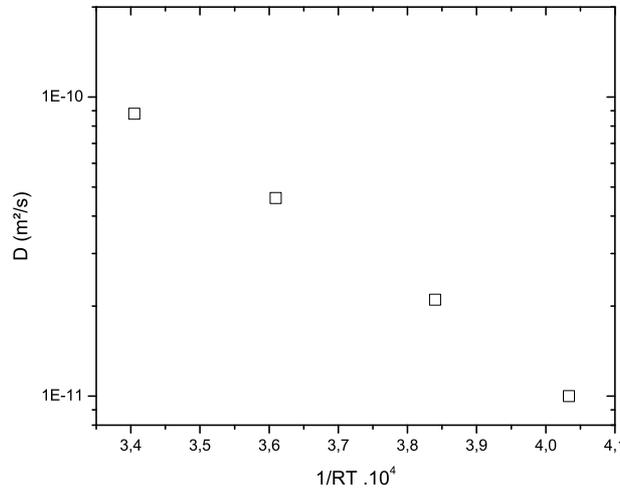

Figure 4: Effect of temperature on water diffusion coefficient

For higher temperature (above 80°C) water diffusion characterization is not possible here due to two facts. The first one is practical, it is not possible to open the ageing tank easily for short term measurements, whereas water up take is very fast (less than 5 hours at 110°C for a 2mm thick sample). To overcome this difficulty it would be interesting to increase the characteristics time of diffusion using thicker samples, but this is not possible here because sample mass decreases when degradation occurs due to leaching of degradation products (figure 5) [22] [23].

Because water diffusion characterization at high temperature (more than 80°C) is not possible, values at these temperature will be extrapolated based on an Arrehnius law as shown in figure 4.

As a conclusion on water diffusion in PU, it is possible to describe water diffusion in this material using Ficks equation where D is related to water
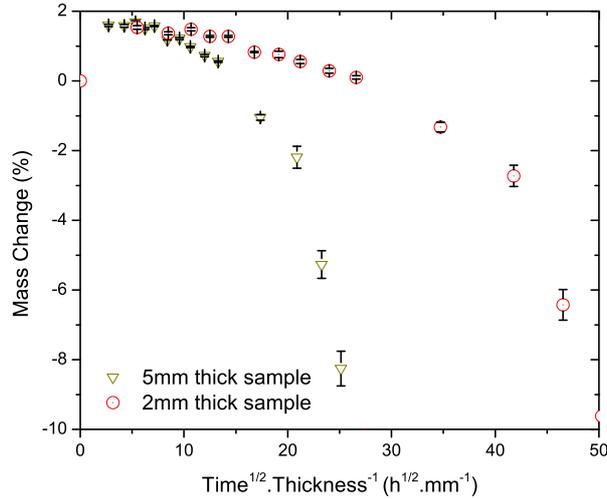
Figure 5: Mass change during ageing at 100°C in sea water

temperature by an Arrhenius law. In this case the pre-exponetial factor is equal to $1.15 \, 10^{-5} \, \text{m}^2$ /s and the activation energy is 34.5 KJ/mol. The next section will be dedicated to irreversible degradation in PU due to water and temperature.

3.2. Polymer degradation

Tensile characterization

Figure 6 shows the evolution of tensile behaviour of PU with duration of ageing at 100°C in sea water.

Degradation leads to a large modification of tensile behavior of the material, in fact a decrease of modulus is observed with ageing time due to chain breakage in the polymer. Evolution of ultimate properties (strain and stress at break) as function of ageing duration for different temperatures is plotted in figures 7 and 8.

Whereas temperature leads to an increase in degradation kinetics it seems that the effect of degradation on mechanical properties is the same for all temperatures, i.e. an increase of elongation in the first stage of degradation and then a large decrease. At the same time, stress at break decreases significantly when hydrolysis occurs. The next section will propose a model of
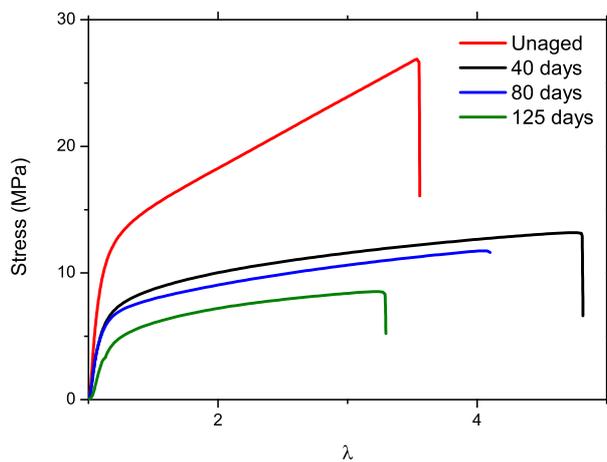
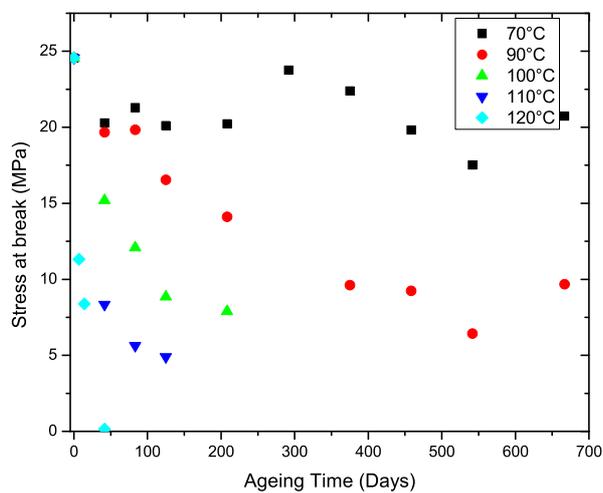Figure 6: Evolution of tensile behavior after ageing at 100°C in sea water for different ageing durations

Figure 7: Elongation at break change during ageing in sea water for temperature from 120°C to 70°C
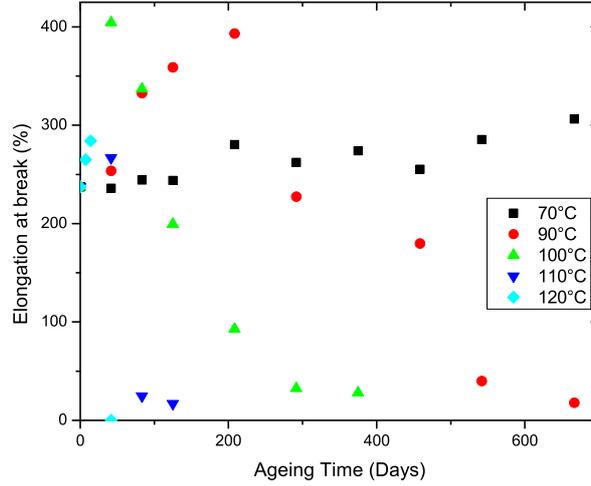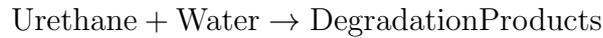
Figure 8: Stress at break change during ageing in sea water for temperature from 120°C to 70°C

the urethane hydrolysis, which is necessary to make life time prediction of the thermal insulation layer used on pipes.

Degradation modelling

Reactions in figure 1 can be simplified as the following equation:

$$Urethane + Water \rightarrow DegradationProducts$$

Hydrolysis of the urethane bond in water at high temperature leads to chain scissions in the polymer. In this case, the kinetics of chain scission can be written as follows:

$$\frac{dn}{dt} = k.[H_2O].[U] \tag{4}$$

where n is the number of hydrolysis events, $[H_2O]$ concentration of water in the polymer, $[U]$ concentration of urethane linkages and k kinetics of reaction.

In this study, samples are 2mm thick to ensure that water diffusion is much faster than hydrolysis and so degradation is not controlled by diffusion.

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In fact the characteristic time for diffusion can be calculated according to equation 5 [24] [25]:

$$\tau = \frac{L^2}{D} \tag{5}$$

Where D is water diffusion coefficient in m^2 /s and L sample thickness in m. Characteristic times of diffusion for each ageing temperature are reported in 1. For all temperatures, the time necessary to hydrolyse the material is much longer than the time for water to diffuse inside the polymer sample; this is a clear indication that degradation is not limited by water diffusion.

Sea water temperature	Characteristic Time for diffusion (Days)
70	0.7
90	0.4
100	0.3
110	0.2
120	0.2

Table 1: Characteristic times of water diffusion in PU at different temperatures

In this case, water concentration in the sample is a constant, thus equation 4 can be rewritten:

$$\frac{dn}{dt} = K.[U] = K.([Uo] - n) \, where \, K = k.[H_2O] \tag{6}$$

From equation 6 and using analytical resolution it is possible to show that

$$\ln \frac{[Uo] - n}{[Uo]} = -K.t \tag{7}$$

To assess the value of K for all ageing temperatures, a change of urethane linkage during degradation is needed; in this case this value comes from uniaxial tensile tests. In fact when considering an elastomer without reinforcing fillers, the stress-strain curve is directly related to crosslink density of the material through the equation [26] :

$$\sigma = \rho.RT.(\lambda - \lambda^{-2}).\nu \tag{8}$$

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where σ is tensile stress, ρ is sample density, R is the perfect gas constant, T is testing temperature in Kelvin, λ is elongation and ν the cross link density (i.e. number of urethane bonds in a specific volume) in mol/Kg. This relation is true for low deformations.

As a result it is possible to evaluate the number of hydrolysis events based on the evolution of crosslink density with ageing time and so determine the value of K. Figure 9 show the evolution of the logarithm of the normalized stress as a function of time, this evolution is linear, which validates the assumption of a first order reaction. From the slope, it is possible to assess kinetic constants for each temperature.
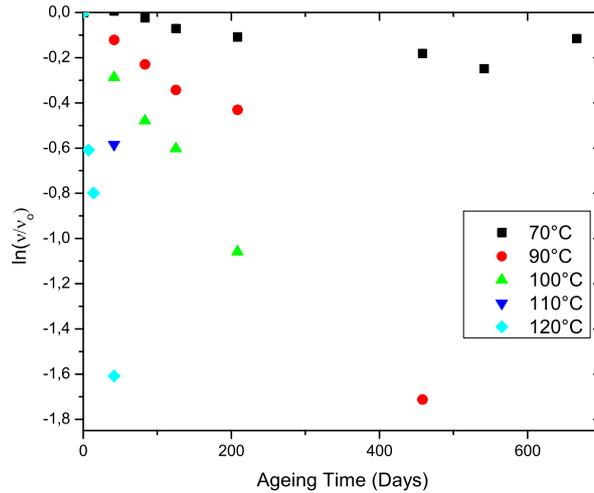

Figure 9: Assessment of the K value for different ageing temperatures

The temperature dependence of hydrolysis is plotted in figure 10. Within the temperature range of 70 to 120°C hydrolysis kinetics follow an Arrhenius behaviour with activation energy of 115KJ/mol.

Based on equation 7 and results obtained here it is possible to model the urethane degradation when it is used in contact with sea water at high temperature. The reliability of this prediction depends largely on the validity of the equation that describes the temperature dependence of hydrolysis kinetics. In fact although utilization of Arrhenius behavior in polymer
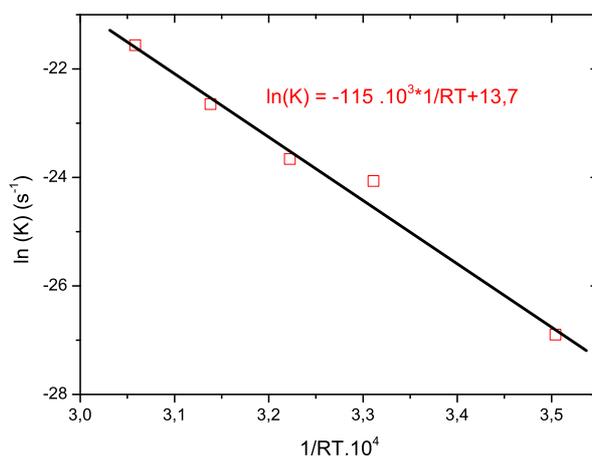
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Figure 10: Temperature dependance of the hydrolysis kinetics K

degradation is controversial [27] [28] [29] [30], nevertheless in this case our approach is different. In fact usually accelerated ageing is usually performed at high temperatures and then degradation is extrapolated back to service temperature which is lower, assuming an Arrhenius behavior over the whole temperature range. Here, ageing is performed at a temperature close to the service conditions and so there is no need for extrapolation of kinetics to low temperature. In order to valid the prediction, results obtained by modeling have been compared to experimental data obtained on a real structure that has been aged for more than a year (to be published).

4. Conclusion

A commercial polyurethane based on polyether has been aged for more than a year in natural sea water from 25°C to 120°C. Water diffusion and degradation kinetics have been evaluated using weight change and tensile characterization. When immersed in sea water, this PU absorbs about 1.8% of water and undergoes hydrolysis at high temperature. Hydrolysis leads to chain scission in the polymer and so induces a large modification of tensile behaviour. In fact stress at break decreases significantly when degradation occurs. At the same time an increase of elongation at break is observed initially, followed by a drastic drop. The hydrolysis reaction of polyurethane

has been modeled using a first order reaction with an Arrhenius equation to describe temperature dependence. Using data from this study, it is now possible to set up a coupled model for water diffusion and polyurethane hydrolysis in a topcoat used as thermal insulation for oil extraction flowlines.

Acknowledgements

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