Material performance

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.

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 the sea to production plant situated on the 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, a 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 [1–3]. 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. Therefore, it is 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 the 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. PU based on polyester undergoes fast hydrolysis even at low temperature in water [4–7] 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 [8–11]. Nevertheless, under very severe

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conditions the urethane linkage can undergoes hydrolysis. The chemical reactions involved in this degradation have been identified under both acidic and basic conditions [12–14]. All these authors found that, in polyether based PU, the most labile bond is the urethane one. Chemical reactions during hydrolysis can be written as in Fig. 1 [14–16]:

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.

2. Experimental details

2.1. Material

The sample studied here is a commercial polyether-based polyurethane widely used for passive thermal insulation. It 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 the Brest estuary and was renewed every day to avoid any contamination by degradation products. For temperatures above 95 °C, ageing was performed under hydrostatic pressure (100 bars).

2.3. Weight change

The water diffusion was determined from the weight evolution of square samples (50 mm * 50 mm) 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 to dry the surfaces before weighing. The mass change (M) of each sample at time t is expressed as a percentage as:

$$M(t) = \frac{m(t) - m_o}{m_o} \cdot 100 \tag{1}$$

where $m(t)$ is sample mass at time t and m_o 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, 2 mm 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 stored for 24 h 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

Fig. 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.

Typical Fickian behavior is observed in Fig. 2, at the beginning of immersion, water up take is directly proportional to the square root of time normalized by sample thickness and then, for longer durations, a plateau is reached [19–21]. Utilization of two different sample thicknesses is very useful to check that water absorption follows Fickian behavior.
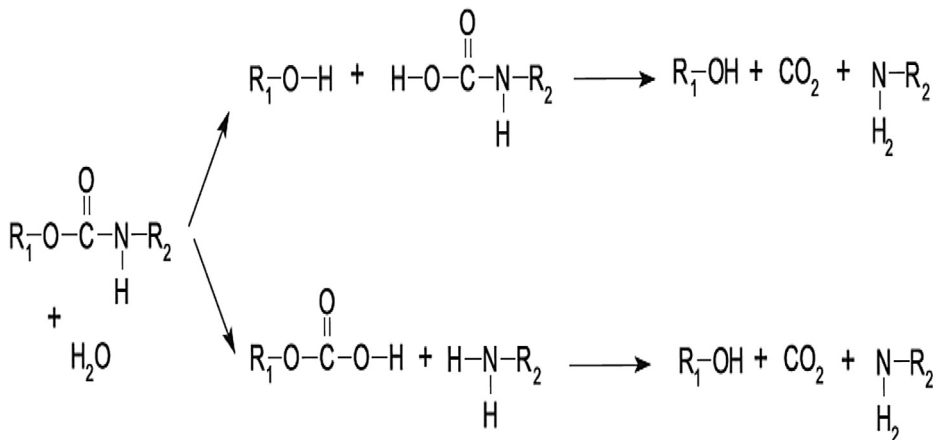

Fig. 1. Chemical reactions involved in urethane hydrolysis.