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Material Properties

Characterization of seawater and weather aged polyurethane elastomer for bend stiffeners

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ABSTRACT

A bend stiffener grade polyurethane (PU) elastomer was physically and mechanically characterized by attenuated total reflectance Fourier transform infrared spectroscopy, thermogravimetric analysis and tensile tests. The material was then exposed to artificial seawater and weather up to 12 months to evaluate its stability as bend stiffeners are exposed to this type of environment during offshore operation. The characterization of aged samples was performed comparing the ageing effects on the chemical structure, thermal stability and mechanical properties with those of the non-aged material. The mass variation of aged samples immersed in artificial seawater was also measured. A slight change in the chemical structure led to a color change from dark green to brown in the samples exposed to natural weathering for 12 months. Increases in thermal stability, stiffness and strength characteristics were also verified, which may be associated to additional crosslink formation. In contrast, a significant mechanical property drop was observed for the artificial seawater aged PU, being attributed to a plasticizer effect induced by the ageing fluid. The stress-strain curves were adjusted with the Mooney-Rivlin model allowing the crosslink density estimation. The weather aged PU presented higher crosslink density than seawater aged and non-aged samples.

1. Introduction

A bend stiffener is an ancillary conical shaped component that locally supports flexible risers to limit bending stresses and curvatures to acceptance levels (API 17J [1]). It ensures smooth stiffness transition between the flexible riser and floating production unit, avoiding riser damage due to stochastic environmental loading. The device is usually manufactured with ether-based polyurethane elastomer and is exposed to harsh environments, such as seawater or seawater atmosphere, solar radiation and a wide range of temperatures, among others (Bazan et al. [2], Opera [3], Murata et al. [4]).

Some key parameters for a proper bend stiffener design, which currently leads to a highly insulating structure, are the environment (water or air) and pipe operational temperatures. During normal operational conditions in air, the outer surface is exposed to solar radiation and the inner surface to heat transfer from the pipe flow. During full-scale fatigue tests, the polyurethane is subjected to high loading rates required to accelerate the decades long operational conditions. As a consequence, more energy is dissipated (viscoelastic) and the structure temperature increases. Doynov et al. [5] has recently observed a bend stiffener failure due to overheating during a full-scale fatigue qualification test. The thermal analysis performed resulted in a maximum temperature close to 75 °C, which was higher than the maximum allowable. Due to higher rates of heat transfer, lower operational temperatures are expected for the PU in water. However, as the seawater ageing mechanism may have a greater impact in the mechanical response than weather exposure when operating in air, it does not implicitly translate into a safer operation. Consequently, a better understanding of the bend stiffener PU behavior aged in seawater and exposed to the weather, in conditions similar to those observed during operation, is essential for a safer design.

Polyurethane elastomers are very versatile materials whose properties can be tailored for specific applications and to work in different environments by the simple choice of a proper

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combination of reagents: diisocyanate, which can be an aromatic or aliphatic monomer, polyol, normally ester or ether, and a small molecule chain-extender, in the presence of suitable catalysts and additives (Prisacariu [6]).

Few research can be found in the literature on the ageing of polyurethanes for marine applications. PU samples were subjected to accelerated ageing in artificial and natural seawater for different time periods in the work presented by Davies and Evrard [7]. They reported mechanical properties drop due to a plasticizer effect induced by the ageing fluid. Furthermore, a significant material degradation was observed when the ageing was carried out at elevated temperatures such as 70 °C and above. Other studies associated with polyurethane ageing in seawater are reported by Rutkowska et al. [8], Gac et al. [9], among others. Regarding the weather effect, some studies can be highlighted. Boubakri et al. [10] exposed thermoplastic polyurethane (TPU) to artificial weathering, observing that mechanical properties such as elastic modulus and tensile stress initially decreased and that, after exposure over 6 h, an increase occurred (possibly due to crosslink formation). Other studies about the ageing of polyurethane subjected to artificial weathering have been performed (Liu et al. [11], Rosu et al. [12], Bajsic et al. [13]). According to Liu et al. [11], when TPU films were exposed to artificial irradiation carried out by a xenon lamp, the materials showed a stress drop at the break values and higher elastic modulus as exposure period increased. This is indicative that the material becomes stiffer as irradiation time progresses. Rosu et al. [12] noted a yellowing of the PU surface when irradiation time was increased due to degradation and photooxidation of the CH_2 groups. Bajsic et al. [13] observed that photooxidative degradation was more intensive when PU elastomers presented lower hard segment concentration and higher soft segment molecular weight.

The most common degradation mechanism reported for polyurethanes working in high humidity or underwater environments in severe conditions is hydrolysis, even for polyether-based elastomers, known to be less susceptible to bond breakage. This chemical reaction causes a decrease in the network density and consequent loss of mechanical properties (Gac et al. [9]). The authors have not found any work on bend stiffeners concerning the chemical degradation of the polyurethane relating the ageing of the particular material to its mechanical properties. Most of the works reported on such structures are dedicated to nonlinear mechanical modeling of the material and its effect in the flexible pipe/bend stiffener system response (Sodahl and Ottesen [14], Caire et al. [15]).

Although the previously mentioned works contribute to the knowledge on the behavior of elastomeric polyurethane under marine environment and natural or artificial weather, none of them assessed grades specifically developed for bend stiffeners. Aiming at contributing to the knowledge on the behavior of bend stiffener grade polyurethanes and the effect of aging on the mechanical properties of the material, a MOCA crosslinked polyurethane was aged in artificial seawater at 60 °C and exposed to natural weather to evaluate the chemical resistance of the material in environments similar to the ones encountered during offshore operation. Tensile tests were carried out at room temperature to evaluate the mechanical behavior of aged samples. In addition, the stress-strain curves were employed to obtain an indirect estimation of crosslink densities based on the Mooney-Rivlin model.

2. Materials and methods

2.1. Material

The materials employed in this work were a bend stiffener grade polyurethane and artificial seawater. The polyurethane elastomer was supplied in 3 mm thick plates for the mass variation experiments and 6 mm for the tensile testing, and specimens were machined in the necessary geometries for each different experimental technique. To assess the effect of the various environments in the chemical structure and on the mechanical and thermal behavior of the polyurethane samples, the ageing was performed in artificial seawater (according to ASTM D1141 [16]) at 60 °C during 1, 6 and 12 months, and at natural weather for periods of 6 and 12 months.

2.2. Mass variation

To evaluate weight change of PU and its chemical resistance, specimens with planar geometry were cut with dimensions of 30 mm × 25 mm x 3 mm. The initial mass M_1 of each sample was measured in air using an analytical balance with an accuracy of 0.1 mg. Then the specimens were immersed in artificial seawater at 60 °C and this fluid was renewed every 6 months. At the desired immersion time, a set of three samples was withdrawn from the container, wiped dry with paper towels and the specimen masses measured in air for its average calculation $M_2(t)$. The withdrawn samples were not re-immersed and the total immersion time was intended to characterize absorption saturation. The mass variation $\Delta M(t)$ for each sample was calculated according to Eq. (1) as follows,

$$\Delta M(t) = \frac{(M_2(t) - M_1)}{M_1} \cdot 100 \quad (1)$$

2.3. Attenuated total reflectance fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to verify changes in the chemical structure of the polyurethane elastomer occurred due to seawater and/or natural weather ageing. ATR-FTIR spectra were recorded with a Spectrum 100 Fourier transform infrared spectrometer, employing the ATR technique at a resolution of 4 cm^{-1} and 32 scans in the range of 4000 to 550 cm^{-1}.

2.4. Thermogravimetric analysis

The degradation profile of the aged and non-aged PU samples was assessed by thermogravimetric analysis (TGA) using TGA Q50 V20.10 Build 36 equipment. A mass of approximately 10 mg was heated from environment temperature up to 700 °C at nitrogen atmosphere and heating rate of 10 °C min^{-1}.

2.5. Tensile testing

Tensile tests for artificial seawater and natural weather aged and non-aged PU were carried out on an Instron universal testing machine according to the specifications of ASTM D412 [17]. At least five specimens were tested using a crosshead speed of 50 $mm.min^{-1}$. All the experiments were done at room temperature (23 °C).

3. Results and discussion

3.1. Mass variation

The mass variation $\Delta M(t)$ as a function of time in days is presented in Fig. 1. It shows a fast mass gain followed by a mass