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Limits in the validity of Arrhenius predictions for field ageing of a silica filled polychloroprene in a marine environment

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ABSTRACT

Accelerated ageing in natural sea water at different temperatures from 20 °C to 80 °C was performed on a silica filled polychloroprene rubber. Degradation when monitored with mechanical properties at both macroscopic and microscopic scale led to a large increase of the modulus coupled with a strong decrease of strain and stress at break. Data from tensile tests were used for lifetime prediction with an Arrhenius extrapolation for modulus, strain and stress at break. The validity of this lifetime prediction was evaluated using a 23 year-old sample aged in natural conditions. Strain at break could be predicted using an Arrhenius extrapolation with an activation energy of 50 kJ/mol. However, an extrapolation based on linear Arrhenius behaviour did not apply for modulus and stress at break due to the presence of a degradation profile across the sample. These observations confirmed that strain at break is not governed by bulk properties of samples but by the degradation rate at the external surface of the sample (*i.e.* in contact with water).

1. Introduction

A clear understanding of ageing processes is crucial to guarantee the long term durability of a new product or to reduce the frequency and thus the cost of maintenance operations. This is a challenging task because ageing is a complex phenomenon that covers a broad spectrum of multidisciplinary domains including the definition of accelerated ageing tests, the identification of the ageing mechanisms, the evaluation of the consequences on the mechanical properties and finally the simulation of real components that integrate the gradients induced by ageing [1]. In order to keep reasonable test and product development durations, accelerated ageing is mandatory. The most common approach to accelerate ageing uses elevated temperature tests combined with an Arrhenius type extrapolation to predict the value of a given parameter for lower temperatures and longer times (see for example ISO standard test method 11346 for rubbers [2]). The Arrhenius extrapolation is widely used for lifetime prediction of polymers in different environments [3–5]. This common application is due to the fact that this approach is easy to perform and can be, in some cases, relevant. Nevertheless, Arrhenius extrapolation in the field of polymer degradation exhibits some limitations and many authors reports that temperature effects on degradation kinetics can not always be described using the Arrhenius equation [6,7,4]. Several factors are involved but two major reasons can be emphasized. First, when the chemical reactions involved in polymer degradation vary between high temperature and low temperature, it is not possible to extrapolate degradation kinetics using a simple time/temperature superposition [7,4]. However, this can be overcome by using a mechanistic approach of the degradation [8,9], which relies on a description of each chemical steps involved in the overall degradation. Second, when degradation involves the diffusion of a reactive component from the external environment to the bulk of the material, non uniform ageing in the polymer thickness with depth can occur. This phenomenon is due to a competition between diffusion and reactive consumption; when diffusion is faster than reaction, then degradation is uniform in the sample thickness whereas when reaction is faster than diffusion then the resulting degradation is non uniform [10–14]. When degradation is not uniform with depth, an extrapolation of macroscopic properties using the simple Arrhenius time/temperature equation will obviously not be relevant; in this case only edge information can be relevant.

Dealing with the marine ageing of rubbers, many studies have been published [15–19], but very few articles investigate the consequences of a marine environment on polychloroprene rubber

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(CR) [20] and none consider possible degradation profiles. This conclusion results from the good resistance of rubbers to this kind of environment [21,15]. The results by Ab-Malek and Stevenson [16], Pegram and Andrady [17], Oldfield and Symes [18] or more recently Davies and Evrard [5] show that after very long periods of exposure, the behaviour of the studied materials remains almost identical to that of the unaged one. For all these reasons, there is a lack of experimental data allowing the establishment of Arrhenius extrapolation for marine aged rubbers [3,5] and very few naturally aged rubber parts to check the relevance of these extrapolations have been examined [16]. Moreover, when naturally aged samples are available, results are rarely compared to accelerated ageing results.

The aim of this paper is to evaluate the influence of marine ageing on the mechanical behaviour of a polychloroprene rubber, both at macroscopic and microscopic scales, and to compare the predicted lifetime (using a linear Arrhenius behaviour) to data from a naturally aged sample (a 23 year old offshore floating export line). First, we present the experimental details, and describe the material used here and the accelerated ageing protocols that are necessary to evaluate the ageing consequences at laboratory time scale. Experimental devices used here to evaluate the evolution of the mechanical behaviour are also presented. Second, we present the experimental results. Finally, a comparison between the results obtained from the accelerated ageing tests and the naturally aged ones is presented.

2. Experimental details

2.1. Material

This study is focused on a filled polychloroprene rubber used as a coating of offshore floating flow lines. The composition of the material is given in Table 1 and the main mechanical properties are given in Table 2. It is worth noting that there is no silane coupling agent in the formulation. In order to perform accelerated ageing, square plates of 2 mm thickness and 250 mm width were manufactured by an industrial partner from the same material batch, in order to ensure the reliability of mixing and moulding conditions.

2.2. Natural ageing

The naturally aged sample originated from the coating layer of an offshore floating export line. This flow line was used in the Atlantic Ocean (near the Cameroun coast) for 23 years at 10 m depth. Sea water temperature varies from 15 °C to 25 °C in this area during the year and pH is around 8.2. The flow line was still meeting the structural mechanical requirements after its withdrawal from service. This naturally aged sample is 2.3 mm thick and meant to protect the structure from any environmental degradation, and did not reveal any visible damage after its service life. The compound used for the accelerated ageing tests has exactly the same formulation as the one used in the flow line.

Table 1
Formulation of the studied material.

Components	Content (phr)
Chloroprene rubber	100
ZnO	6
MgO	4
plasticizer	<10
Carbon black	6
Silica	46
Stearic acid	2
Antioxidants	2
Accelerators	1

Table 2
Main mechanical properties of the studied material before ageing.

Properties	Values
Density	1.4
Hardness (Shore A)	68
Microhardness [MPa]	3.2
π_{rupt} [MPa]	17.4
ε_{rupt} [%]	670

2.3. Accelerated ageing

In order to be as close as possible to the service conditions, specimens were immersed in several tanks filled with natural sea water coming directly from the Brest estuary and maintained at different temperatures for different durations (cf. Table 3). Water was continually renewed using a peristatic pump leading to the replacement of the vessel volume (60 L) every 24 h without any modification of the temperature. 2 mm thick plates were removed periodically from the tanks.

During the accelerated ageing, the samples will absorb some water according to diffusion mechanisms [21], leading to an increase in mass and volume. Even if no dramatic effects on the mechanical behaviour are expected [21], a reversible effect is generally noted in rubber modulus [22]. Unfortunately, the dependence of the mechanical behaviour on both the ageing degradation and the amount of water absorbed by the material does not allow for an objective comparison between various ageing conditions easy. To be able to compare the various ageing conditions, we chose to focus on dried samples. To be as unintrusive as possible, the samples were dried at 40 °C in an inert atmosphere (N_2 gas) until a constant weight was reached. This drying protocol was optimized and validated by a specific study detailed elsewhere [23].

2.4. Tensile tests

After the ageing and drying steps, the samples were cut from the sheets with a punch die in order to obtain normalized dumbbell shapes (type 2 from the standard ISO 37:2005). The choice to age sheets rather than dumbbell samples originates from the difference in the diffusion processes. Dealing with samples cut from sheets, the gradients will be 1D with only variations along the thickness and not along the width (as it would have been if dumbbell samples were aged), which is clearly easier to manage. The tensile tests were performed on a Lloyd LR5K+ testing machine, equipped with a 1 kN load cell. The tests were displacement controlled with a grip speed of 10 mm/min. A laser extensometer LASERSCAN200 was used to measure the true strain during testing. For each ageing condition, at least three samples were tested and the results averaged. In this paper strain and stress are related to nominal values, *i.e.* both values are calculated based on initial parameters (length and section). In this paper three values will be considered: strain at break, stress at break and M100 which is modulus at 100% *i.e.* the stress at this elongation.

Table 3
Exposure times [days] for thermally accelerated ageing under water immersion.

20 °C	40 °C	60 °C	80 °C
–	–	16	16
–	30	–	30
50	50	50	50
–	–	–	79
172	172	172	172
–	381	381	–
526	526	–	–
686	–	686	–