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Fatigue behavior of natural rubber in marine environment: Comparison between air and sea water

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A B S T R A C T

Natural rubber has been successfully used in a marine environment for many years. However, most applications involve low dynamic loadings. Due to the emergence of marine energy recovery, wave and tidal energy converters are being developed. In some such devices, rubbers are subjected to severe cyclic loadings, very different from their previous use in air or water. Such rubbers must therefore be qualified for long-term use in sea water with high fatigue loading. This paper presents a study using a new fatigue machine that allows the fatigue behavior of rubber in sea water to be compared to that in air. The results show that the benefit of non-relaxing conditions on fatigue lifetime of natural rubber can be significantly reduced when it is used in sea water, observed in particular for a ratio of minimum to maximum strain of $R = 0.2$. In order to understand this new result, the effects of both antioxidant and of minimum strain during the fatigue cycle were investigated. The effect of antioxidant was found to be the same in sea water and air, i.e. an increase of the stabiliser level leads to an increase in fatigue life, so it appears that antioxidant leaching is not the origin of the reduction of fatigue life in sea water. It was noted that this reduction of number of cycles to failure does not occur when natural rubber is used in sea water in fully relaxing cycles, suggesting that strain induced crystallisation, responsible for the beneficial effect of non-relaxing cycles on fatigue resistance, might be adversely influenced by sea-water at a ratio R of minimum to maximum strain equal to 0.2.

1. Introduction

World energy demand is steadily increasing, and although recent shale oil and gas discoveries have increased reserves these are not unlimited. Sooner or later alternative sources of energy will be needed, and renewable energy sources are of particular interest. These are defined as those coming from any resource which is naturally replenished on a human timescale. Because the oceans represent more than 70% of the earth's surface there has been a particular interest in marine renewable energy, and many new concepts of energy converters from waves, tidal or temperature gradient are now available. In order to ensure economic viability of such energy converters, reduced maintenance and long term durability of these structures in this severe environment is of major interest.

Durability of structures in a marine environment depends critically on both design and material. Polymers and composites are widely used at sea, driven by the desirability of weight reduction and avoidance of metal corrosion. Durability of polymers and composites in sea water has been widely studied in the past mainly for subsea oil and gas extraction [1–4] and for military purposes [5]. However, for most of these applications mechanical loading is usually either static or, if dynamic, with low stress or strain amplitudes. This is no longer the case when considering marine energy converters, particularly wave energy converters [6–8], which need to undergo large movements in order to operate. In order to manage the fatigue issue, material selection tends to the use of rubbers when possible, and natural rubber in particular as it has unsurpassed fatigue resistance in air because of its capacity to crystallize at high strain [9–12].

Natural rubbers are already used in marine structures and show good long term behavior. In fact, if the material is well formulated water absorption is low (about 1%) and does not significantly affect quasi static mechanical properties [13–16]. It is worth noting however, that rubbers are complex formulations and the choice of additives and fillers is very important when considering their long term behavior [17,18]. But the main outstanding question is about the fatigue behavior of such materials in a marine environment and in particular, does the good fatigue behavior of NR in air change when

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immersed in sea water. Mott and Roland [19] studied the effect of ageing of NR in sea water compared to ageing in air on properties, including fatigue life, measured subsequently in air and concluded that the behavior is the same, and due to oxidation. However, they did not investigate fatigue behavior of immersed rubber. Fatigue of natural rubber immersed in distilled water has been performed by Lake and Pond in fully relaxing load cycles [20]; the results were not fully resolved for unprotected rubber (i.e. without stabilization), water immersion led to an improvement of fatigue life for low strain, probably because of the lack of ozone attack underwater. For protected samples no difference between water and air was observed. However, in their study a large water absorption was observed (up to 10%), because the osmotic balance was tipped in favour of water absorption, there being no solutes in the water, and the rubber, being unfilled, had a low elastic modulus. The absorbed water formed blisters in the rubber, since it is very sparingly soluble in polyisoprene, but the blisters evidently are not effective fatigue initiation sites. More recently Selden [21] studied the effect of immersion on crack propagation in NR and concluded that there was a little effect, especially at low crack growth rate.

Based on data from the literature it would thus be expected that immersion of natural rubber in sea water will not greatly affect its fatigue lifetime, but more evidence is needed, covering materials and duty cycles more relevant to the conditions proposed for wave energy converters; this is the main objective of the current study.

To study the effect of sea water immersion on fatigue behavior of natural rubber a new fatigue rig was developed and will be presented in the first part of this paper. Testing conditions were chosen carefully in order to avoid self-heating of samples, to evaluate lifetime with a large number of samples per condition and to use a well-known rubber formulation. The second part of this paper will be devoted to the comparison of fatigue behavior in air and sea water under non-relaxing conditions. The third part will focus on the origins of the effects observed, and in particular the decrease in lifetime for rubber in sea water, together with an investigation into the effect of stabilizers in the formulation and the effect of the minimum strain.

2. Material and methods

2.1. Rubber formulation

The materials used in this study are carbon black-filled natural rubbers whose compositions are shown in Table 1. The main characteristics of this compound, albeit with a different antidegradant or stabilizer system, can be found in the Engineering Data Sheets [22]. In order to study the effect of antioxidants on the fatigue lifetime, three rubber have been formulated with different levels of stabilization called A, B and C.

2.2. Water absorption

The water absorption was determined from the weight evolution of square samples (50*50 mm) with a 2 mm thickness immersed in natural sea water renewed at 4 L/h at 25 °C. 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:

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

where $m(t)$ is sample mass at time t and m_o is the dry sample mass (the initial weight of material prior to water exposure) before immersion. For each condition (temperature, pressure and thickness), 3 samples were weighed to ensure the reliability of the measurement.

Table 1
Formulations of the rubbers used in the study.

Ingredients (pphr)	EDS14A	EDS14B	EDS14C
NR	100	100	100
Carbon black	15	15	15
Process oil	1.5	1.5	1.5
Zinc oxide	5	5	5
Stearic acid	2	2	2
Accelerator	0.6	0.6	0.6
Sulfur	2.5	2.5	2.5
Antioxidant 2246	0	1	2

2.3. Fatigue tests

2.3.1. Samples

Fatigue tests were performed using dumbbell samples with a thickness of 2 mm and a type 2 shape according to the ISO Standard 37:2011 [23]. There were three main reasons for this choice; the first is to avoid self-heating in the samples, in order to use the same thermal conditions in both air and sea water, so the use of thick diabolo specimens was not possible here. Secondly, the use of test-pieces bonded to end fixtures was thought to risk the complication of bond failure (e.g. underbond corrosion) limiting the lifetime. Finally, total break of type 2 dumbbells is a convenient end of life criterion for monitoring in these tests [24].

2.3.2. Fatigue machine

Experiments have been conducted on a fatigue test facility developed at Ifremer in which seven replicate specimens can be tested. It is composed of an electrical displacement controlled piston PRA3810S from Parker piloted by a computer. Maximum force and frequency available during a cycle are respectively 1860 N and 7 Hz. Fig. 1 shows one of the machines developed for this study.

The main aim of the study is to see whether or not sea water has an influence on the fatigue life of rubber. Tests were performed in

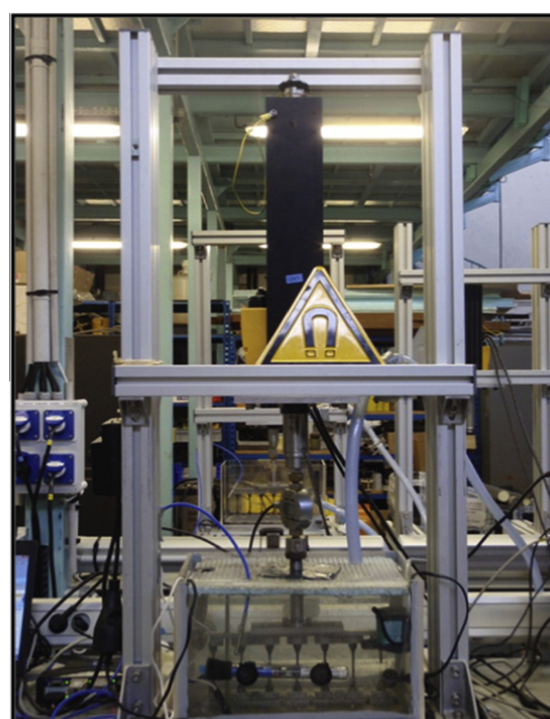

Fig. 1. Testing machine developed at Ifremer.