International Journal of Fatigue 88 (2016) 247–256

Contents lists available at ScienceDirect

International Journal of Fatigue

journal homepage: www.elsevier.com/locate/ijfatigue

Fatigue resistance of natural rubber in seawater with comparison to air

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ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 30 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Natural rubber
Fatigue
Environmental effects
Seawater
Strain-induced crystallization

ABSTRACT

Fatigue properties of filled natural rubber in seawater environment are investigated by uniaxial fatigue and crack propagation experiments, and the damage is analyzed by scanning electron microscopy. The behavior under relaxing and non-relaxing loading conditions is studied and the results are compared to those obtained in air environment. For relaxing loading conditions, fatigue behavior is the same in both environments. Under non-relaxing conditions at large strain levels, for which the influence of strain-induced crystallization is important, fatigue life is longer in seawater. Such behavior could be explained by increased internal temperatures of specimens tested in air due to lower heat conductivity of air as compared to seawater. Such conclusion is also supported by the damage mechanisms observed under non-relaxing loading conditions.

1. Introduction

Natural rubber (NR) is a versatile elastomer that has been used industrially for well over a century. It has found use in many different applications mainly because of its ability to dissipate energy and undergo large elastic deformation whilst maintaining excellent resistance to crack growth. The majority of NR is used in production of automobile tires. Additionally, it finds use in the marine environment (upon a selection of appropriate formulations) because of its low water absorption and consistent mechanical properties after prolonged immersion in seawater. With recent growth of interest in off-shore energy production, ranging from oil or natural gas, wave, wind to tidal energy, better understanding of fatigue behavior of natural rubber in seawater is of interest at present.

The study of NR fatigue is divided into two complementary approaches that lead to determination of fatigue life [1]: the crack nucleation approach, which focuses on the prediction of crack initiation in a material without defects; and, the crack propagation approach, which considers the cyclic growth of an existing crack. The crack nucleation approach refers to continuum mechanics, whereas the crack propagation approach refers to fracture mechanics. Several factors influence fatigue properties of NR. In general, they are separated into three groups [2]: mechanical loading conditions, environmental conditions, and chemical formulation (addition of antioxidants, antiozonants, fillers, and other additives used in the industrial process).

The mechanical loading conditions for soft materials are usually defined by prescribed displacement or strain energy density [3]. In both cases, we classically define the *R*-ratio, or the loading ratio, as the ratio of the minimum to the maximum loading quantity. In terms of the stretch ratio $\lambda = l/l_0$, it is defined as:

$$R = \frac{(\lambda_{min} - 1)}{(\lambda_{max} - 1)} \tag{1}$$

The *R*-ratio is a useful descriptor of mechanical loading and its value considerably affects the fatigue behavior. For $R = 0$, i.e. the minimum loading quantity is zero, the mechanical loading conditions are said to be relaxing; when $R > 0$, i.e. the minimum loading quantity is positive, they are said to be non-relaxing. Under the latter type of loading conditions, fatigue resistance of NR improves (notably in contrast to metals). The general consensus is that presence of strain-induced crystallization (SIC) is responsible for such improvement [4,5]. The effects of SIC in fatigue will be discussed in further detail in Section 4. For further information on SIC in rubber, the reader can refer to the review articles of Tosaka [6] and Huneau [7].

The second factor that influences fatigue properties of rubber is the environment. In air, the fatigue behavior has been extensively studied: see for example Cadwell et al. [8], Rivlin and Thomas [9], Lindley [4,10], Lake [11], and many others. In air, fatigue is a mechanico-oxidative process [12]. Comparison with results in an oxygen free environment (nitrogen) reveals that gaseous oxygen accelerates crack growth and decreases the fatigue crack propagation threshold [13]. A study by Gent and Hindi [14] shows that in

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http://dx.doi.org/10.1016/j.ijfatigue.2016.03.033

Nomenclature

6PPD	*N-[1,3-Dimethylbutyl]-N′-phenyl-p-phenylenediamine* (antioxidant, antiozonant)
c	crack length of a SENT specimen
CB	carbon black
CBS	*N-cyclohexyl-2-benzothiazolesulphenamide* (vulcanization accelerator)
k	constant as a function of maximum stretch ratio relating tearing energy to strain energy density for SENT specimen
l	deformed length
l_0	initial length
EDS	energy dispersive spectroscopy
LVDT	linear variable differential transformer
NR	natural rubber
SENT	single-edge notched tension specimen
SEM	scanning electron microscopy
SIC	strain-induced crystallization
R	loading ratio
T	tearing energy
W	strain energy density
λ	global stretch ratio
$\Delta\lambda$	amplitude based on maximum local stretch ratio
λ_{local}	maximum local stretch ratio within the specimen
λ_{max}	maximum amplitude based on maximum local stretch ratio
λ_{min}	minimum amplitude based on maximum local stretch ratio

vacuum environment, i.e. with no exposure to oxygen, the crack propagation rate is reduced roughly by a factor of 2 as compared to air environment. Oxygen also has a long term effect on NR fatigue due to aging, which is driven by diffusion of oxygen in NR; primarily, it affects the mechanical properties making it hard and brittle [15]. For NR, aging reduces the fatigue life, fastens crack propagation, and reduces fatigue threshold [1].

In contrast, effects of seawater (or water in general) on NR fatigue have not been investigated to the same extent as in air. Mott and Roland [16] carried out accelerated aging experiments and found that the concentration of oxygen in seawater has a direct effect on degradation of NR. As for fatigue behavior, under relaxing loading conditions ($R = 0$), one study suggests that fatigue crack propagation rates are almost identical to the ones in air [17]. Moreover, after a long-term immersion in seawater of 2.25 years, no difference (compared to air) in crack propagation properties has been observed for $R = 0$ [17]. Additionally, it has been shown that fatigue life under relaxing loading conditions is similar in distilled water [18] and in seawater [19] as compared to air. On the other hand, under non-relaxing loading conditions at $R = 0.2$, the fatigue threshold is higher and crack propagation is slower in water compared to air regardless of temperature [13]. In the recent study of Le Gac et al. [19], a decrease in fatigue life is observed in seawater compared to air under non-relaxing loading conditions; this result is obtained for filled NR (15 phr of carbon black) with and without antioxidants. Moreover, it appears that antioxidant leaching has no effect on fatigue life of NR in seawater [19].

In the present paper, the focus is primarily on mechanical loading and environment. Since fatigue properties of NR are relatively well-understood in air, the objective is to compare these properties in seawater; an important question is whether the vast knowledge of fatigue behavior in air can be expanded to the seawater environment. The present work parallels the study of Le Gac et al. [19], specifically, to a greater range of strain levels under which the beneficial effects of strain-induced crystallization are greatly enhanced. Both fatigue life and fatigue crack propagation experiments are carried out, and the corresponding damage mechanisms are observed by scanning electron microscopy (SEM).

2. Experimental program

2.1. Material

The composition of the studied material is given in Table 1. The material is molded into sheets of 2 mm uniform thickness and the specimens are cut using a die and a pneumatic press. The experiments are performed on a virgin material and no pre-aging steps are considered.

2.2. Specimens

Fatigue life tests are performed on flat dumbbell specimens (H3) with dimensions shown in Fig. 1 (ISO 37:2005 standard, dumbbell: type 3). In the middle of the specimen, the gauge length is 17 mm long and the stress state is that of uniaxial tension. Fatigue crack propagation tests are performed on single-edge-notched tension (SENT) specimens shown in Fig. 2; the dimensions are 146 mm × 25 mm × 2 mm and a 1 mm cut is introduced in the middle of the specimen with a brand new blade. The design of the experimental grips reduces the effective length of H3 and SENT specimens to 28 mm and 96 mm respectively.

2.3. Experimental procedure

Actual fatigue tests are performed on custom-built electrically driven machines (actuators *Parker* PRA 3810S). The testing machines apply a sinusoidal waveform that is displacement controlled. The sinusoidal movement of the actuators is verified manually (minimum and maximum positions) and by using an LVDT. Tests are performed in both air and seawater environments. The loading ratios $R = 0$ and $R = 0.2$ are considered. These values are calculated considering the local maximum stretch ratio λ_{local}. All fatigue experiments are performed at 2.0 Hz. Experiments in air are carried out at laboratory room temperature, i.e. 22 °C. For the experiments in seawater, specimens are submerged into home-made tanks (12 L in volume). The seawater is extracted directly from the roadstead of Brest and its properties are shown in Table 2. Seawater is continuously renewed by slow drainage and addition of extra seawater; the rate of water flow through the tank is in the order of magnitude of 1 L/h, which does not affect the temperature that is held constant at 25 °C by using a thermocouple-controlled heater. Water is aerated and its closed circulation is managed by a pump. The seawater is replaced for each test. The experimental setup for fatigue life tests is shown in Fig. 3.

Before the fatigue experiments, the Mullins effect is removed by performing 50 cycles at 110% of the maximum local stretch ratio prescribed in fatigue experiments. The frequency of these accommodation cycles is set to 0.5 Hz and a 15 min long relaxation period is imposed between accommodation and start of the fatigue experiments.

2.3.1. Preliminary tests

The maximum local stretch ratio λ_{local} differs from the prescribed global stretch ratio due to sample geometry. Here, the local stretch ratio is measured by digital image correlation (DIC). The material stress–strain response and the details of the DIC experiments are expanded in Appendix A. Additionally, experiments