
Marine durability of carbon black-filled polychloroprene: effect of seawater ageing on network, tensile and fatigue properties

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Abstract :

With the development of marine renewable energies, the durability of materials at sea is more than ever a major issue in reducing the risk of failure of offshore devices. In this aggressive environment, elastomers, and in particular polychloroprene (CR), have many applications because of their good damping and fatigue properties. However, these materials are subject to ageing in service, which leads to changes in their mechanical properties. The ageing of these materials in a marine environment has not been extensively studied, despite the need to predict components lifetimes. This paper investigates the mechanical and microstructural consequences of a carbon black-filled CR degradation when exposed to seawater. To this end, swelling, uniaxial tensile and fatigue tests are carried out on materials previously subjected to accelerated ageing in natural seawater. Particular attention is paid to understanding the physico-chemical phenomena involved, and analysing fracture and fatigue properties in relation to those of the macromolecular network.

Highlights

► Exposition to seawater leads to changes in polychloroprene mechanical properties ► Important seawater absorption softens the material without affecting extension at break ► Irreversible degradation leads to crosslinking in the macromolecular network ► Relationships link macromolecular network and mechanical properties during ageing ► These relationships are independent of the ageing temperature and environment

Keywords : Polychloroprene, Seawater, Ageing, Fatigue, Structure-property relationships

1. Introduction

The emergence of marine renewable energy is becoming increasingly important, making it a viable option for reducing our dependence on fossil fuels. Elastomers are essential materials for offshore structural parts, because they provide the necessary flexibility and resilience to withstand harsh ocean conditions. In particular, polychloroprene rubber (CR) is frequently used in various applications such as coatings, fenders or membranes for its excellent fatigue and damping properties [1] [2] [3]. However, when exposed to environmental conditions, CR, like other rubbers, is prone to physical and/or chemical ageing, resulting in changes of performances.

Studies on ageing of elastomers have been conducted since the 1950s, first focusing on the oxidation of natural rubber [4] [5]. Polychloroprene has received particular attention in recent decades, and its response to thermo-oxidative ageing in air is now well established. Its degradation scheme has been experimentally determined through H-NMR [6] [7] and FTIR [8]: radical reactions attack double bonds, creating new crosslinks. These techniques, supplemented by measurements of oxygen consumption rates [9], have also been used to investigate the kinetics of the crosslinking process [10]. As the reactions progress, the network becomes increasingly crosslinked by new intramolecular covalent bonds, reducing the length of elastically active chains [11]. From a macroscopic point of view, this results in an increase in stiffness, with significant consequences on the mechanical response of the material. Moreover, the ability of the elastomer to withstand large deformation is reduced, which leads to a decline of strain at break under quasi-static loading conditions [12] [13], and an alteration in strain-induced crystallisation

(SIC) [14]. Investigations in dynamic conditions show an increase in energy dissipation with increasing crosslink density [15], as well as a reduction in fatigue life [16] [17].

Despite the utter importance of materials durability for offshore applications, few studies have looked at elastomer ageing in marine environments. Generally speaking, polymers (including elastomers) absorb water when immersed [18] [19]. As water absorption is a reversible phenomenon, it is referred to as physical ageing. In addition, chemical reactions that modify the network can also take place within the material, influenced or not by the presence of water: this is known as chemical ageing. The difficulty lies in the fact that material degradation is a combination of both types of ageing. Consequently, in order to gain an exhaustive understanding of these phenomena and their respective contributions, it is necessary to carry out two types of characterisations on aged materials. On the one hand, tests on wet aged materials enables the observation and quantification of the overall degradation. These tests are the most frequently carried out, as they reflect the actual properties of materials during their use in service: for instance fracture properties [20] [21] and tear resistance [22] [23] of salt water-filled CR have been investigated. However, these tests do not clarify the contribution of water absorption to total mechanical degradation. On the other hand, in order to separate the phenomena, it is necessary to remove physical ageing, to indirectly assess the effect of water. This aspect has been rarely studied in the past, mainly for silica-filled CR [24] [25], where water hydrolyses the silica, but to the best of our knowledge, never for carbon-black filled CR.

Another unanswered question is the effect of seawater ageing on the fatigue properties of CR. Dynamic tests have been recently carried out in seawater on unaged elastomers to study cracking [26] and the effect of formulation [27]. However, the studies have never been extended to predict the fatigue life of samples aged in seawater, which is essential as it is often a decisive criterion in the design of offshore structures.

In this article, we carry out seawater ageing at several temperatures on a carbon black-filled polychloroprene. The aged samples are then tested, both wet and dried, in order to characterise seawater absorption, changes in the macromolecular network and the mechanical properties, including tensile and fatigue. The adopted approach consists in decoupling physical and chemical ageing, in order to analyse the reversible or irreversible nature of degradation in seawater. Finally, to predict fatigue and fracture performances, relationships between network and mechanical properties are proposed for the first time for a filled CR in a marine environment.

2. Materials and methods

2.1. Material

The material is a 15 phr carbon black-filled polychloroprene, widely used in marine applications. Its formulation is presented in Table 1. It has been vulcanised for 10 min at 170°C, and is supplied as thin sheets of dimensions 250 mm x 250 mm x 2 mm.

Table 1 : Material formulation

Compound	Per hundred rubber
Polychloroprene type W	100
Carbon black HAF N330	15
Sulfur	1.875
MgO	4
ZnO	5
Stearic acid	0.5

2.2. Seawater ageing and drying

Prior to ageing, the material undergoes one week of anaerobic maturation at 100°C to produce the material referred as ‘unaged’ (see [17] for more details). Then, ageing is performed at different temperatures in tanks of natural seawater, as shown in Figure 1a. The seawater, which is pumped directly from the Brest bay (on the French Atlantic coast), is continuously renewed while maintaining constant temperatures of 25°C, 40°C and 60°C. Samples are fully immersed in seawater, which is considered as a transfer medium in equilibrium with the ambient atmosphere. In this scenario, although the solubility of O₂ differs between air and seawater, the partial pressure of oxygen in seawater remains theoretically equal to that at the surface in air. Denote C_{CR} as the concentration of O₂ at the surface of an immersed CR sample, S_{CR} as the solubility of O₂ in CR, P_{CR} as the partial pressure of O₂ at the CR surface, and P_{air} as the partial pressure of O₂ in ambient air. The concentration of O₂ is therefore given by the relation $C_{CR} = S_{CR} \times P_{CR}$. When seawater is in equilibrium with the surrounding air, P_{CR} equals P_{air} , implying that the concentration of O₂ absorbed by the material is the same as in air, even though the concentration of dissolved O₂ is lower in seawater. This assumption is adopted in our work. The impact of water pressure is not considered here, although higher hydrostatic pressure could influence O₂ permeation through seawater and the material’s response to ageing. Table 2 details the ageing durations considered for mechanical testing. Note that supplementary ageing conditions are taken into account for seawater absorption.

Table 2 : Ageing conditions

Ageing temperature (°C)	Ageing durations (days)					
25°C			90	190	341	502
40°C	10		90	190	341	502
60°C	10	61	90	190		

In this study the materials are tested wet, i.e. as they come out of the tanks, and dried. The drying method consists in 3 days of anaerobic exposure at 100°C, in a vacuum drying oven. It was verified that this process does not induce additional degradation.



Figure 1 : a) Seawater tank facilities used to perform accelerated ageing. b) Custom fatigue experimental setup in seawater, adapted from [26].

2.3. Experiments

This section describes the characterisations carried out on the materials during ageing, with particular attention to their condition (wet or dried). For all figures, the error bars correspond to the minimum and maximum values.

2.3.1. Seawater absorption

In order to determine seawater uptake during ageing, square samples of CR measuring $50 \times 50 \times 2 \text{ mm}^3$ were initially weighted, then immersed in the seawater tanks. Their mass m_{air} is regularly measured on a Sartorius weighing scale, with a precision of $\pm 0.1 \text{ mg}$. Furthermore, their buoyancy in water m_{water} is measured with an immersed weighing scale device [28]. According to Archimedes' principle, the volume of the sample V is

$$V = \frac{m_{\text{air}} - m_{\text{water}}}{\rho_{\text{water}}},$$

Equation 1

where ρ_{water} is the water density. The volume uptake Δ_V is calculated relative to the initial unaged state: $\Delta_V = (V_{\text{aged}} - V_{\text{unaged}}) / V_{\text{unaged}}$. Three samples are weighted regularly per ageing temperature.

2.3.2. Swelling tests

Swelling tests are performed on dried materials in accordance with ISO-1817 [29]. Three samples per ageing condition are considered. The average crosslink density ν is calculated according to the Flory-Rehner theory [30]

$$\nu = -\frac{1}{V_{\text{tol}}} \frac{[\ln(1 - \nu_p) + \nu_p + \chi \nu_p^2]}{\nu_p^{\frac{1}{3}} - \frac{\nu_p}{2}},$$

Equation 2

where $V_{\text{tol}} = 106.3 \text{ mL.mol}^{-1}$ is the molar volume of toluene, ν_p is the volume fraction of the swollen rubber, and χ is the Flory-Huggins parameter set to the standard value for CR [31]; χ is considered independent of ageing. Note that as the rubber is filled, ν is an apparent crosslink density, encompassing intramolecular crosslinks and matrix/filler bonds [32].

2.3.3. Tensile tests

Uniaxial tensile tests are performed in accordance with ISO-37 [33]. H3 flat dumbbell samples are tested at room temperature (20°C). An INSTRON 5966 machine is used, along with a 10 kN load cell and a laser extensometer to measure the strain ε (in %). Extension λ is defined as $\lambda = 1 + \varepsilon$. The tests are conducted at constant quasi-static extension rate $\dot{\lambda} = 10^{-2} \text{ s}^{-1}$.

For wet samples at a given ageing condition, a correction factor $(1 + \Delta_V)^{1/3}$ is applied to the nominal stress, to account for the seawater-induced swelling of the samples [34]. Consequently, the nominal stress P in uniaxial tension is

$$P = \frac{F \times (1 + \Delta_V)^{1/3}}{S_0},$$

Equation 3

where F is the measured force and S_0 the undeformed section of the sample. For dried samples, $\Delta_V = 0$, no correction is necessary and Equation 3 reduces to $P = F / S_0$. In any case, 3 samples are tested per condition.

2.3.4. Fatigue tests

The fatigue experiments are performed with a displacement-controlled, custom-built machine. A preliminary chart establishes the equivalence between applied displacement and the unaged sample extension. Seven ISO-37 H3 samples are tested simultaneously. All tests are carried out in fully relaxing conditions at a strain loading ratio $R = 0$ and a sine frequency of 2 Hz. Before the tests, the Mullins effect is removed by 100 cycles at 100% strain, followed by 15 min of relaxation at 100% strain. Image recording is used to identify the number of cycles that corresponds to the catastrophic failure of the sample, which is considered as the end-of-life criterion.

On the one hand, fatigue tests of wet samples take place in a 12 L plexiglas tank, shown in Figure 1b. The seawater is renewed by slow drainage, while maintaining a constant temperature of 20°C. On the other hand, dried materials are tested in air at room temperature, similarly than in [17].

3. Results and discussion

This section presents the experimental results of seawater ageing and their interpretation. The analysis follows three steps:

- Evaluation of the impact of seawater exposition on mechanical properties,
- Investigation on the origin of degradation,
- Discussion on the correlation between the mechanical properties of aged materials and their macromolecular network.

3.1. Effect of seawater ageing on the ‘service’ properties of CR

First, let us assess the effect of seawater exposition on the CR properties. In this section, the materials are tested in their **wet** state, immediately upon removal from the tanks. It is representative of their service conditions.

3.1.1. Seawater absorption

The material absorbs seawater when immersed, resulting in an increase in volume Δ_V shown in Figure 2. The horizontal axis is \sqrt{t}/e , a convenient scale for diffusion processes, where t is the time (in h) and e the samples thicknesses ($e = 2$ mm). We observe a large seawater absorption of the elastomer, reaching up to 120% in volume after approximately two years at 60°C. As already observed on CR, there is no absorption saturation, presumably because of water clustering inside the samples. This phenomenon, driven by osmotic processes [35], has first been described by Fedors [18] [36], and could be explained by the solubilisation of additives (such as vulcanisation, stabilisation or reinforcement agents) used in the rubber formulation. If they are partially soluble in water, a solute layer can form in a droplet at the additive surface. This solute has its own osmotic pressure, which differs from the one of the external medium, typically close to zero. As a result, the seawater uptake is now driven by the difference in osmotic pressure between clusters and external seawater, rather than by concentration differences. Moreover, it appears that the seawater absorption process is limited by the diffusion: Δ_V perfectly correlates with \sqrt{t} . Nevertheless, this behaviour enables precise and thorough interpolation of the stress correction factors that are essential to post-process the tensile tests.

The material’s ionic uptake falls outside the scope of the present paper and warrants further investigations. However, it is noteworthy that, according to the literature, freshwater should induce higher water absorption than seawater [23].

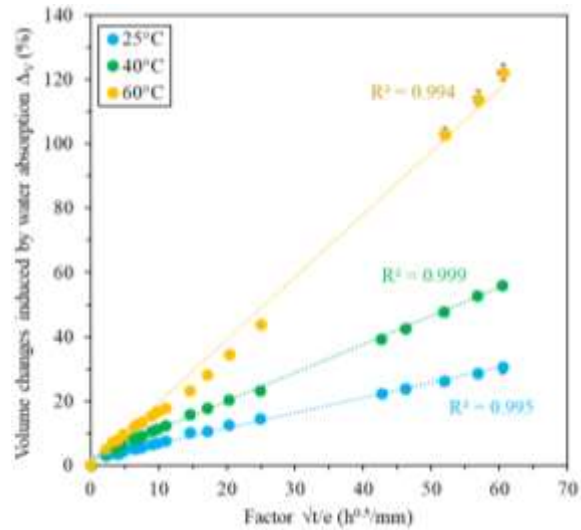


Figure 2 : Volume uptake throughout ageing time due to seawater absorption.

3.1.2. Quasi-static tensile properties

Figure 3 presents the changes of nominal stress-extension curves throughout ageing in seawater, for all ageing temperatures. The unaged material is plotted in black, and aged materials are in shadings of colours.

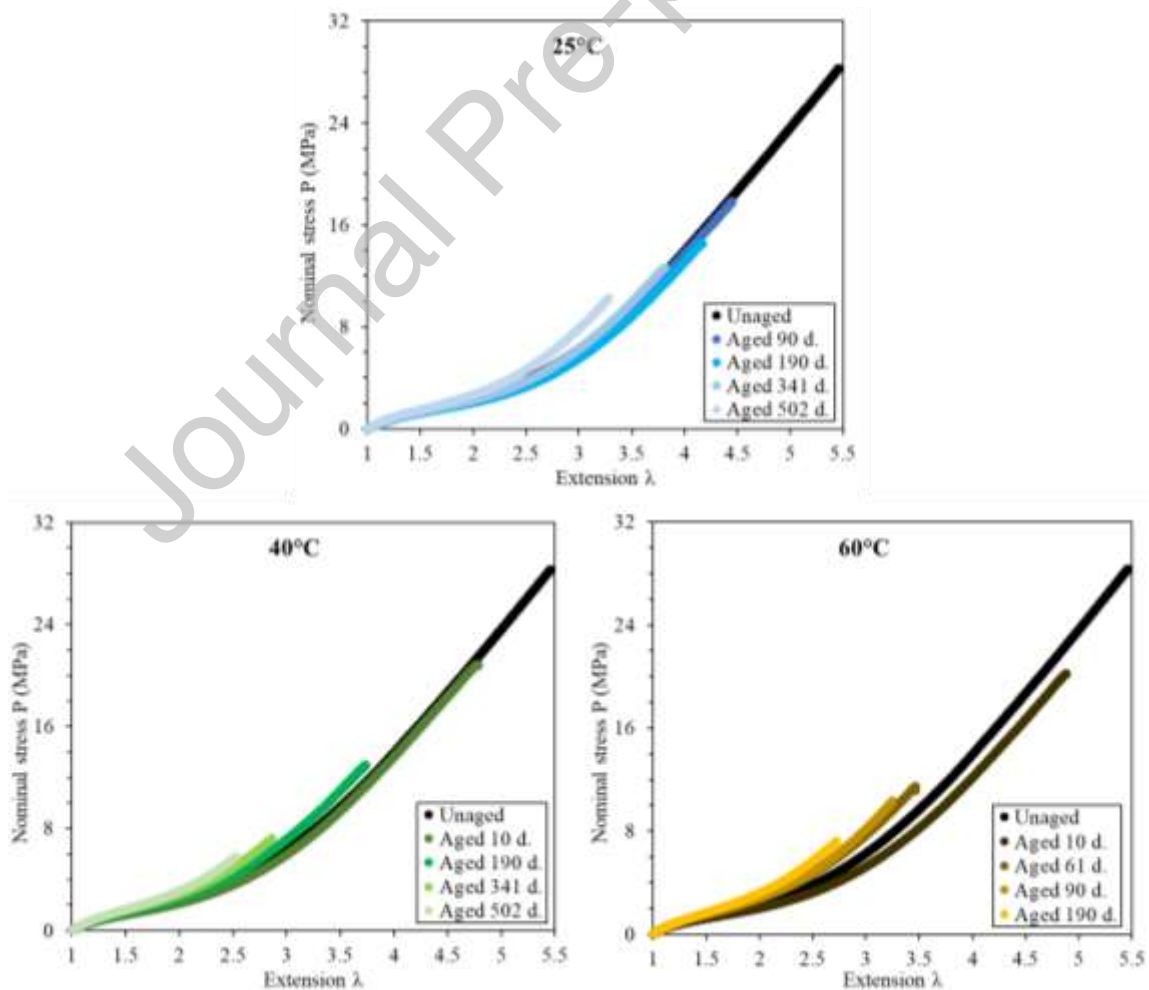


Figure 3 : Nominal stress - extension curves of wet material throughout ageing in seawater, for each ageing temperature.

Ultimate properties decrease considerably, both extension at break λ_b and nominal stress at break P_b . A slight stiffening is also observed: it is quantified by the strain energy density W evaluated at $\lambda=2$

$$W = \int_{\lambda=1}^{\lambda=2} P d\lambda.$$

Equation 4

Figure 4 presents the changes of W , λ_b and P_b through ageing time. As similar trends are discernible, it is suggested that the same processes are responsible for the change of quasi-static properties, independently of the ageing temperature. The origin of the CR degradation in natural seawater is discussed later in this paper.

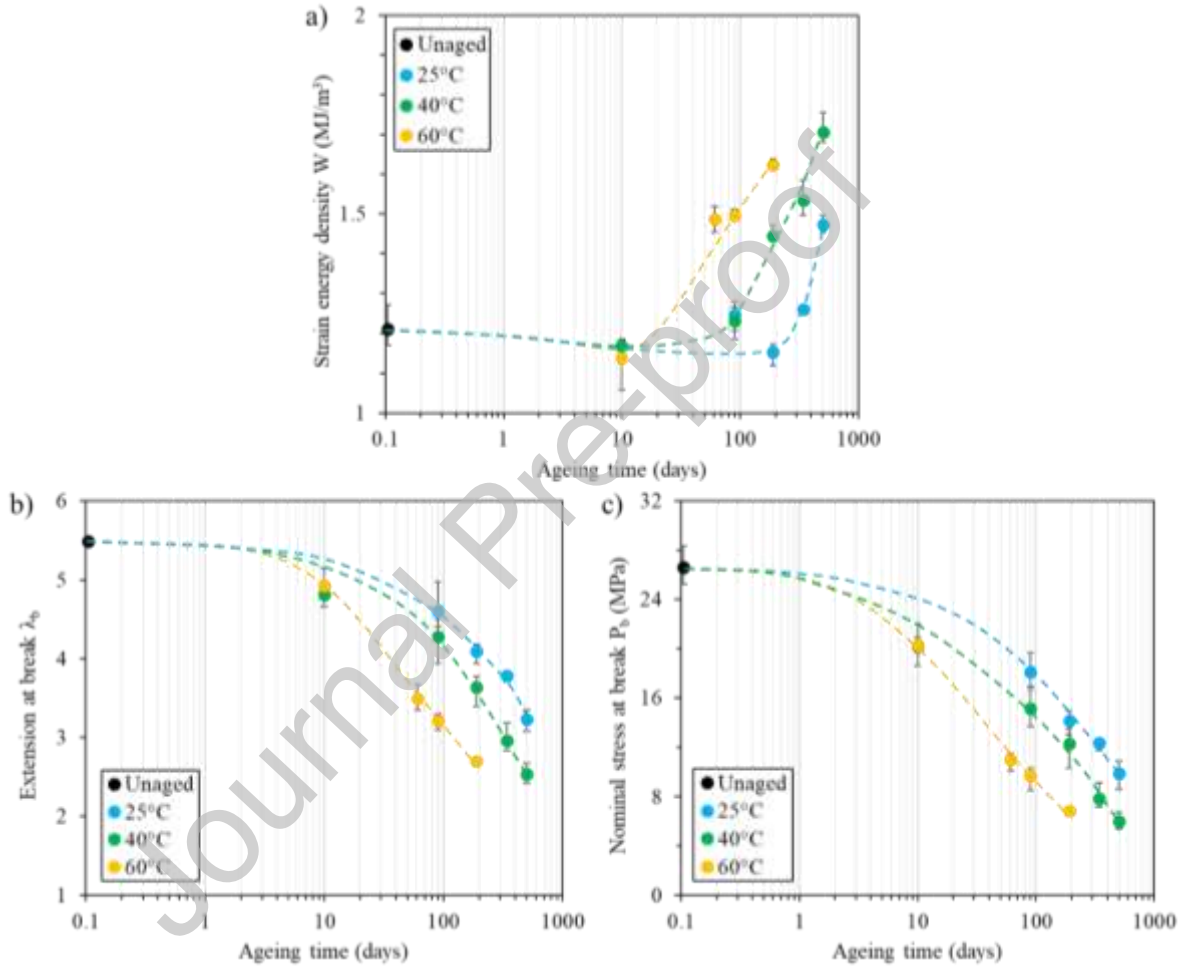


Figure 4 : Change in strain energy density W (a), extension at break λ_b (b) and nominal stress at break P_b (c) through ageing time for all considered temperatures. Dotted lines are guides for the eyes.

3.1.3. Fatigue properties

The Wöhler curve of the unaged material tested in both air and seawater with a loading ratio $R = 0$ is presented in Figure 5. First, fatigue life decreases when raising maximum applied extension λ_{max} . Secondly, mean fatigue lives in air and seawater are very close, indicating there is no impact of the test environment at this loading ratio; this having been already observed for natural rubber [26] [27]. To discuss the effect of seawater ageing on fatigue lifetime, we consider a specific applied extension $\lambda_{max} = 2$, i.e. 100% strain. The according results, displayed in Figure 6, lead to the same conclusions

than the ones of quasi-static loading: there is a temperature-independent drop of fatigue lifetime through ageing, with ageing temperature affecting the kinetics.

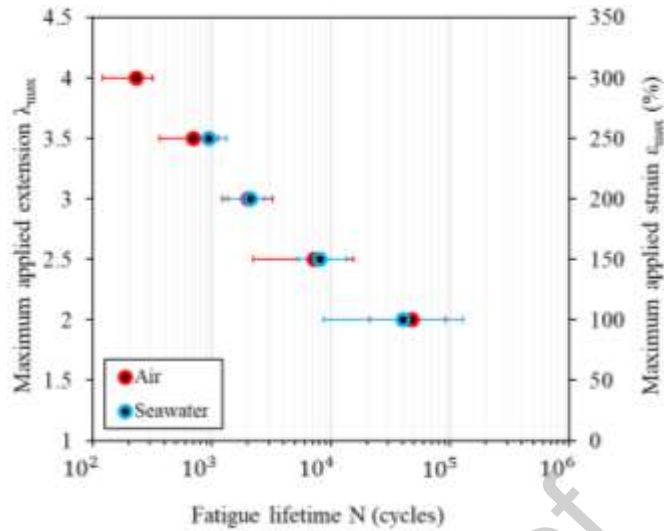


Figure 5 : Wöhler curves of the unaged material in air and in seawater.

To conclude, we have acknowledged a drop of the CR mechanical properties when exposed to seawater (except for stiffness), prompting further investigations to determine the cause of the degradation. Typically, in marine environments, polymers degradation can be physical (reversible) and/or chemical (irreversible). In an attempt to decorelate these phenomena, dried samples are tested to determine whether seawater absorption is the cause of the mechanical properties decrease.

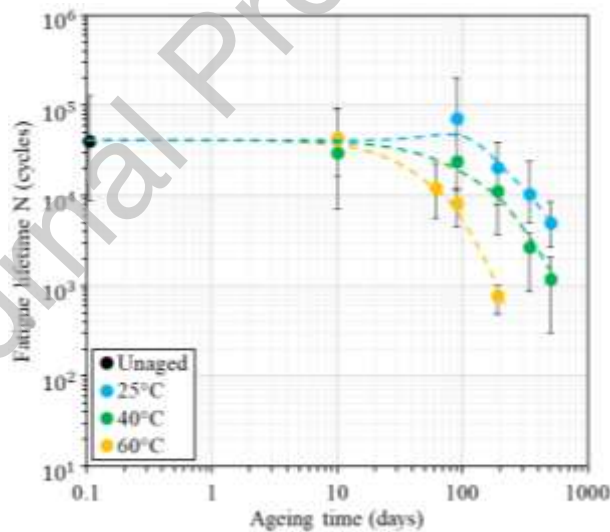


Figure 6 : Drop of fatigue lifetime through ageing time for all considered temperatures ($\lambda_{max} = 2$ and $R = 0$). Dotted lines are guides for the eyes.

3.2. Implications of seawater absorption: evaluating the properties of ‘dried’ CR

In this section, the same mechanical tests as above are carried out on the **dried** samples. By doing so, the reversible effect of seawater is eliminated: only the macromolecular network is responsible for the mechanical response. The objective is to ascertain whether a decrease in properties persists and to understand the effect of seawater on the mechanical response.

The nominal stress-extension curves of the dried material are plotted in Figure 7. Comparing with Figure 3, ultimate properties of the dried material decline during ageing, likewise the wet material. Moreover, the dried material seems to exhibit stiffening as the wet material, yet at a significantly greater extent.

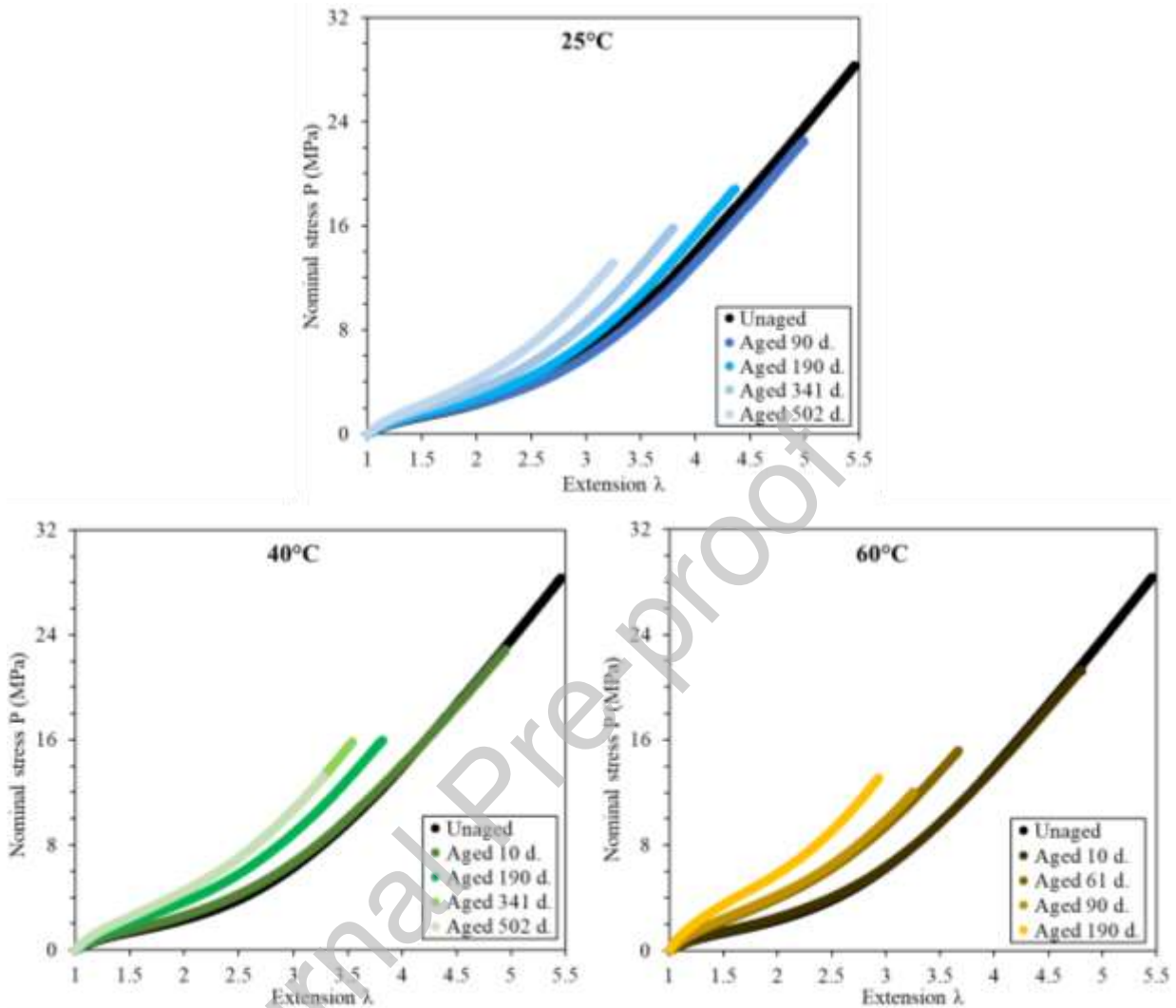


Figure 7 : Nominal stress - extension curves of dried material throughout ageing in seawater, for each ageing temperature.

For each ageing temperature, Figure 8 compares the quasi-static mechanical properties of wet and dried materials; the fatigue life N is only considered for 60°C ageing temperature. This figure sheds light on three features.

- There is a decline in properties of dried material: λ_b , P_b and N decrease during ageing. These trends remain consistent at all temperatures and apply to both quasi-static and dynamic properties. As this drop persists even in the absence of seawater, it indicates that an irreversible process is involved in the decrease in properties. The nature of this process will be examined in the following.
- Extension at break λ_b and fatigue lifetime N are poorly affected by drying. Wet and dried values of λ_b and N are almost identical in the vast majority of cases. Thus, the presence of seawater does not degrade the maximum extensibility of the chains in uniaxial tension beyond the common irreversible process that remains to be determined. This insensitivity to seawater could be explained by the high elasticity of the polychloroprene macromolecular chains. In fact, one possible interpretation is that the chains are able to withstand seawater-induced deformation without undergoing bond breakage. This hypothesis is also supported by the fact that seawater

absorption was not saturated: the material may not have swollen sufficiently for the macromolecules to reach a damaging extension.

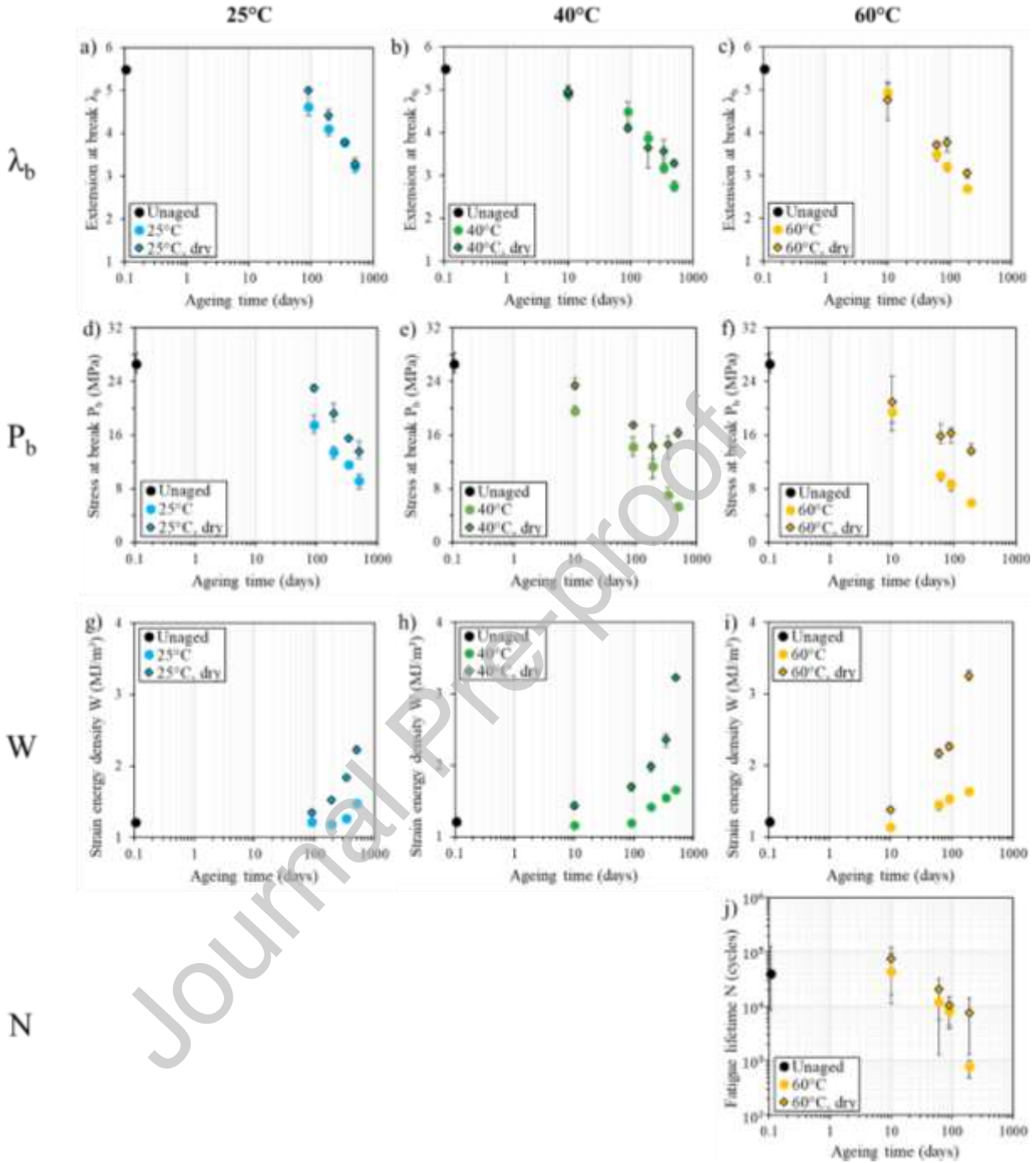


Figure 8 : First row: Wet and dried extension at break λ_b through seawater ageing at (a) 25°C, (b) 40°C and (c) 60°C. Second row: Wet and dried nominal stress at break P_b through seawater ageing at (d) 25°C, (e) 40°C and (f) 60°C. Third row: Wet and dried strain energy density W through seawater ageing at (g) 25°C, (h) 40°C and (i) 60°C. Fourth row: Wet and dried fatigue lifetime N through seawater ageing at (j) 60°C.

- Nominal stress at break P_b and strain energy density W differ depending on whether the material is wet or dried. In fact, these two quantities are linked because the strain energy density is obtained by integrating the nominal stress. Dried materials show higher P_b and W for all ageing conditions: the absorbed seawater seems to act as a softening agent, as already evidenced in previous studies on CR [25]. The particularity here is that this softening effect is superimposed on the irreversible process: the rubber does not recover its initial properties once it has dried.

Qualitatively, the difference between wet and dried material seems to increase with ageing time i.e. the higher the seawater absorption. To discuss this hypothesis, let us consider the ratio between wet and dried strain energy densities at $\lambda = 2$

$$\alpha(\lambda = 2) = \frac{W_{\text{wet}}}{W_{\text{dried}}}$$

Equation 5

The evolution of this ratio is plotted as a function of seawater volume absorption Δ_V in Figure 9: there is a clear reduction in α with absorbed seawater. For $\lambda = 2$, the softening effect appears to be independent of the temperature.

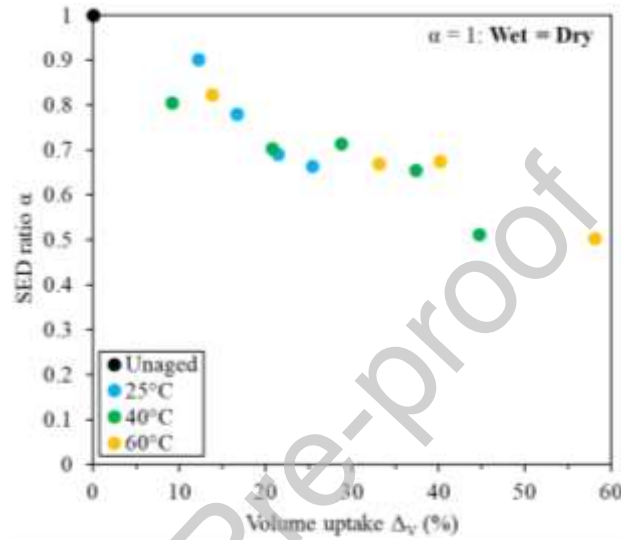


Figure 9 : Correlation between wet/dried strain energy density (SED) ratio and volume uptake, up to the extension $\lambda=2$.

Thus far, it has been established that seawater acts as a softening agent in CR during seawater ageing, affecting stress but not the ultimate extensibility of polymer chains. However, the decrease in mechanical properties during seawater ageing exists even for dried materials, indicating an irreversible degradation of the material. In the following, swelling tests are carried out to elucidate the origin of the degradation at the macromolecular network scale.

3.3. Consequences of seawater ageing at the macromolecular network scale

Swelling in toluene of the dried specimens allows to determine the crosslink density ν , shown in Figure 10. It is clear that crosslinking increases with ageing time, independently of temperature, the latter only influencing kinetics. Therefore, the irreversible chemical degradation of the material during ageing in seawater induces an increase in crosslink density.

This behaviour at macromolecular scale is similar to that resulting from thermo-oxidative ageing of CR in air [16] [37]. However, whereas the degradation mechanism is well known in air [7] [8], it remains an open question in seawater. Although this paper focuses on the effect of seawater ageing on the fatigue properties of CR, the nature of the involved degradation mechanisms is discussed. However, it is important to note that these are hypotheses, and determining the exact degradation mechanisms will require future studies using model polychloroprenes.

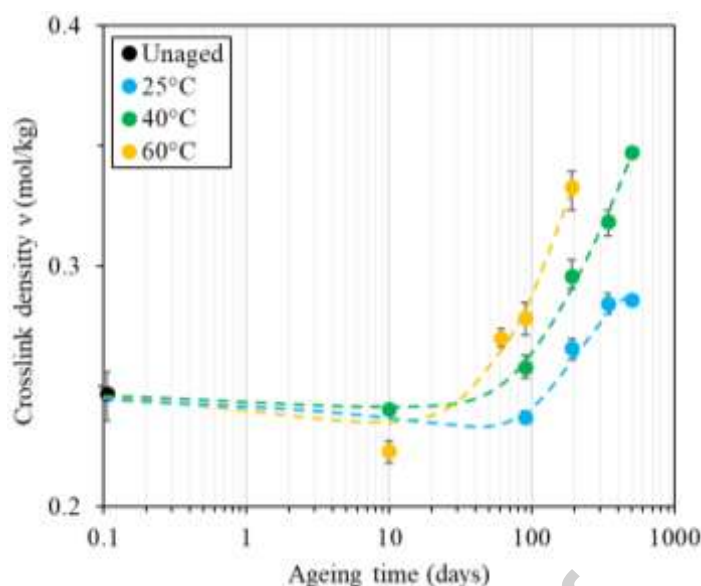


Figure 10 : Change in crosslink density during ageing in seawater. Dotted lines are guides for the eyes.

On the one hand, it seems clear that CR can undergo oxidation in seawater, leading to an increase in the crosslink density because of radical reactions on the double bond [7] [8]. Here, demonstrating the presence of oxidation products by FTIR was not possible due to the presence of carbon black, though this does not imply that the polymer is not oxidised. Exploring oxidation as the potential degradation mechanism, akin to ageing in air, leads to the comparison of activation energies obtained in both air and seawater, while considering changes in extension at break. It appears that the decrease in λ_b follows an Arrhenius behaviour within the range 25 to 60°C, with an activation energy of 44 kJ/mol in air and 37 kJ/mol in seawater, indicating that the activation energies are close in these two environments. Furthermore, the values are in accordance with the ones found by Celina et al. [9] at low temperatures using oxygen consumption measurements. This observation suggests that oxidation might be involved in the degradation process, even though further in-depth studies with model CR should be performed.

On the other hand, it is important to emphasise that the hypothesis of oxidation is not the only one that has been put forth to explain the degradation of CR. Theoretically, if seawater acts as a transfer medium for oxygen, the oxidation rates of an unstabilised polymer in both water and air should be identical, assuming there are no complex diffusion processes between air, seawater the material itself. Yet, the results of degradation kinetics are of concern here: the increase in crosslink density is faster in seawater than in air [38]. For example, at 60°C it takes 90 days for v to increase to 0.28 mol/kg in seawater, whereas this value is reached only after 202 days in air. We propose that this accelerated oxidation may result from two types of interactions with seawater:

- Physical leaching of antioxidants. In air, 6PPD antioxidants are known to migrate within the material by diffusion [39]. However, as 6PPD molecules are polar, and therefore soluble in water, they might migrate to aqueous phases, as demonstrated by recent studies in fresh water [40] [41]. In this case, the solubilisation of 6PPD in seawater could explain faster oxidation in seawater than in air.
- Influence of surrounding chemicals. Furthermore, other naturally occurring chemicals present in seawater might accelerate the oxidation reactions, or lead to concurrent reactions annihilating the antioxidative properties of the elastomer. These factors could help explain why the material experiences faster crosslinking in seawater.

If these hypothesis are confirmed, it raises concern about the suitability of antioxidants 6PPD in formulations designed for use in seawater, because as well as having poor efficacy in this environment, they are highly toxic to aquatic organisms [42] [43].

A comprehensive understanding of the degradation mechanisms governing polychloroprene behaviour in seawater requires ageing tests under controlled oxygen concentrations, as performed in [44]. To this end, CR samples will be immersed in deoxygenated seawater, created by bubbling nitrogen through the seawater to eliminate dissolved oxygen. This method will serve as a baseline for evaluating ageing effects in the absence of oxygen. Concurrently, ageing tests will be carried out in seawater with a controlled oxygen concentration, maintained by regulating a gas layer at the seawater's surface. This setup will simulate oxygen levels found in marine environments. By employing this dual approach, we aim to clarify how oxygen concentration influences polychloroprene degradation, offering valuable insights into its durability in marine applications.

To summarise the potential degradation mechanisms in seawater, it appears that oxidation occurs alongside complex interactions with seawater. This irreversible chemical degradation leads to an increase in crosslink density of the macromolecular network. Our aim is now to derive reliable, formulation-independent descriptors of the material behaviour throughout seawater ageing.

3.4. Structure-properties relationships uniting network and mechanical changes

Considering that the crosslinking of the network can be predicted by kinetic models, we investigate the relationships between ν , λ_b and N , so that long-term change in mechanical properties can be related to the macromolecular degradation of the material.

First, we examine the validity of the relationship developed by Lake [45] when applied to ageing in seawater. In the context of the rubber elasticity theory, relevant for unfilled elastomers [46], extension at break λ_b relates to crosslink density by $\nu^{-1/2}$. This relationship has been verified for thermo-oxidative ageing of unfilled CR [16], and extended to carbon-black filled CR for a large range of fillers content [12] [47]. Figure 11 shows the application of this theory to our experimental data during seawater ageing. Grey points correspond to the structure-property relationship obtained for the same material during thermo-oxidative ageing in air [38]. Note that this representation excludes the degradation kinetics.

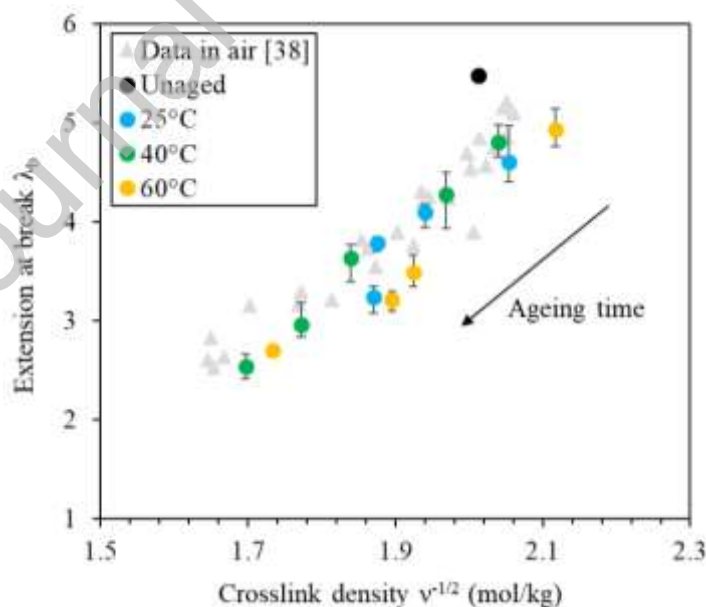


Figure 11 : Relationship between extension at break λ_b and crosslink density $\nu^{1/2}$ during seawater ageing.

From this correlation, extension at break λ_b can be related to the macromolecular network during seawater ageing, independently of the ageing temperature. This original behaviour applicable to low seawater temperatures avoids the use of empirical Arrhenius extrapolations, which may be irrelevant for durability predictions [48] [21]. Furthermore, the structure-property relationship is consistent with

thermo-oxidative ageing data, demonstrating its independence from the ageing environment. This widely extends the applicability of the correlation, although the kinetics depend on the environment and the degradation mechanism in seawater remains unknown.

For fatigue, there is no theoretical relationship between network and fatigue life. Nevertheless, empirical correlations have been proposed and verified on different elastomers during thermo-oxidative ageing [17] [47]. With this in mind, Figure 12 relates the fatigue lifetime at $\lambda = 2$ and $R = 0$ with crosslink density ν . The grey points represent the thermo-oxidative ageing in air. Once again, kinetics are excluded.

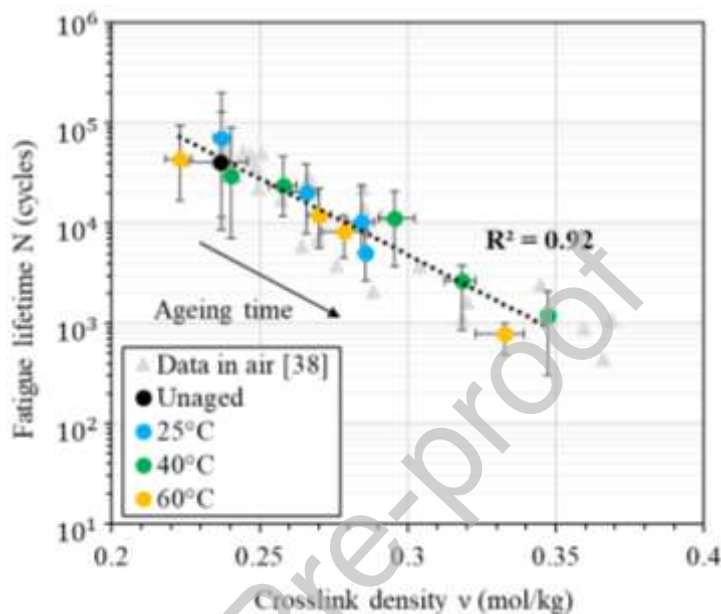


Figure 12 : Relationship between fatigue lifetime and crosslink density ν (at $\lambda=2$ and $R=0$).

The correlation is remarkable, regardless of ageing temperature. Once again, the structure-property relationship is in good agreement with ageing in air, extending its applicability. Nevertheless, future studies will need to validate the relevance of the approach, particularly for loading conditions where strain induced crystallisation significantly impacts the material performance, for example at higher extensions ($\lambda_{\max} > 2$) or for positive loading ratios ($R > 0$).

Finally, extension at break and fatigue life, two crucial design parameters for marine renewable energy components, can be directly related to material crosslinking. It is therefore possible to describe these properties by determining the degradation kinetics only. This is a significant advance for assessing the durability of polychloroprene in oceanic environments.

4. Conclusions

In the present work, ageing of a carbon-black filled polychloroprene in seawater has been thoroughly studied, with considerable effort devoted to its consequences, origin and descriptors. When exposed to a marine environment, the material absorbs large amounts of seawater. This leads to swelling without saturation (i.e. no plateau even after 2 years at 60°C), a behaviour attributed to the formation of water clusters. The absorbed seawater acts as a softening agent, without affecting the maximum extensibility of the chains in uniaxial tension.

One of the major conclusions of this work is that quasi-static and fatigue properties of polychloroprene decrease drastically when immersed in seawater, and even more rapidly than when aged in air. The

irreversible process responsible for the reduction in properties is the crosslinking of CR, although the precise mechanism of degradation is not fully explained here. There is a clear need to further investigate these mechanisms in CR before its deployment in oceanic environments, given the significant reduction in mechanical properties caused by marine ageing.

Structure-property relationships have been established, demonstrating that the extension at break and fatigue life of elastomers aged in seawater can be directly related to the macromolecular network. Furthermore, these relationships are applicable to data from thermo-oxidative experiments in air, suggesting its independence from environmental conditions. However, it is important to note that the kinetics may differ from one environment to another. Determining this kinetics, coupled with our results, would enable to predict long-term durability, a necessity for the design and maintenance of offshore elastomer components. For the future, the complex interconnection between seawater and strain-energy density should be further investigated in order to simultaneously incorporate seawater absorption and crosslinking into constitutive models.

CRedit authorship contribution statement

Hugo Madeira: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing - Review & Editing,

Pierre-Yves Le Gac: Conceptualization, Methodology, Writing - Review & Editing, Supervision.

Maeleenn Le Gall: Conceptualization, Methodology, Writing - Review & Editing, Supervision.

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Declaration of competing interest

The authors certify they have no known interests or personal relationships related to the subject matter or the material discussed in this paper.

Data availability statement

Data will be made available on demand.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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