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Prediction of fatigue lifetime by the strain energy density for filled polychloroprene during thermo-oxidative ageing

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Abstract :

During long-term environmental exposure, polychloroprene undergoes ageing. Throughout the process of thermo-oxidation, chemical degradation leads to crosslinking in the polychloroprene macromolecular network, inducing a significant change in mechanical properties. Among the various consequences of ageing on the properties, the reduction of fatigue lifetime is still poorly understood and needs more accurate prediction methods. This study presents a methodology to relate change in fatigue lifetime loss and network crosslinking during ageing. The material investigated is a carbon black-filled polychloroprene, subjected to more than 25 ageing conditions. Changes in network crosslink density, mechanical strain energy, and fatigue lifetime is experimentally measured. In the present study, a novel prediction strategy is proposed: it relies on the network strain energy density and convincingly describes fatigue loss. As the approach potentially extends to three-dimensional and/or multiaxial problems, it holds promise for addressing ageing-related issues in the analysis of elastomeric parts.

Highlights

► Thermo-oxidative ageing of a carbon black-filled polychloroprene is investigated. ► Ageing causes network crosslinking and drop in quasi-static and fatigue properties. ► Experimental strain energy density matches the theory of rubber elasticity. ► Network strain energy predicts fatigue lifetime independently of the temperature.

Keywords : Polychloroprene, Fatigue, Ageing, Strain energy density

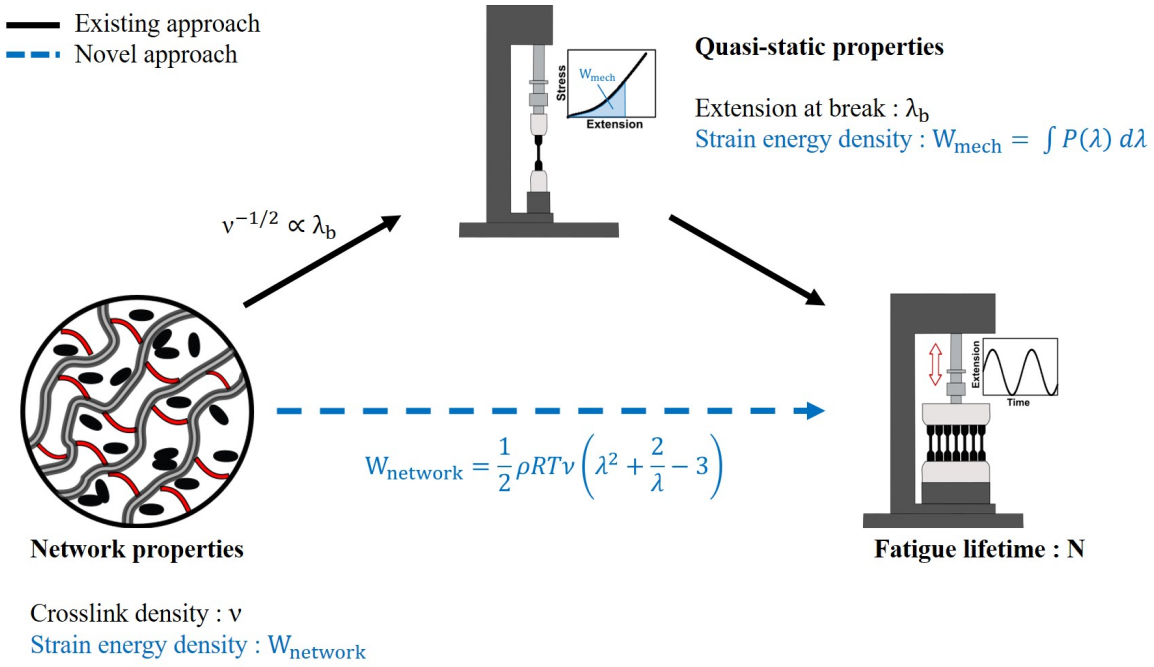

Figure 1: How to relate elastomer network and fatigue properties

1. Introduction

Rubber materials are essential components in numerous industrial technologies, as they provide the flexibility required for parts to bear complex loads. One of the most critical properties is their fatigue resistance, i.e. their ability to withstand repeated mechanical loading when subjected to large deformation. Among elastomers, polychloroprene (CR) exhibits excellent fatigue properties and high extensibility, thus rendering it an optimal material for numerous applications such as shock absorbers, coatings or seals [1, 2, 3]. However, similar to other elastomers, CR is subject to ageing due to environmental exposure. During this phenomenon, it undergoes physical and chemical changes of its macromolecular structure, resulting in degradation of its properties. As mechanical performances drop, material failure is more likely to occur or at least, it leads to a reduced operational time. While significant progress has been made to elaborate CR formulations with enhanced durability, it is critical to ensure the material resilience throughout the parts intended service life.

Ageing in elastomers is strongly influenced by temperature. Generally, lower temperatures are associated with slower ageing rates due to industrial material formulations aimed at mitigating this undesirable

phenomenon. Conversely, elevating the temperature leads to chemical modifications to the macromolecular network, usually referred to as thermo-oxidation. This process has been widely investigated in early research on natural rubber [4, 5], and extended to other elastomers ever since, even for filler reinforced elastomers [6, 7]. For CR, one of the most important degradation mechanism is acknowledged: radical chain reactions occur on the polymer alkene bond, creating new crosslinks [6, 8]. The kinetics of this reaction have been modelled in previous studies for unfilled CR, in accordance with Fourier transform infrared spectroscopy (FTIR) measurements and micro-indentation [9, 10]. Temperature dependence is adequately characterized, including the onset of diffusion-limited oxidation (DLO) effects from a critical temperature. Thus, it is possible to predict crosslink density (usually named ν) during thermo-oxidative ageing.

At the network scale, macromolecules overall mobility is hampered because of intramolecular crosslinks: the length of elastically active chains decreases with ageing. At the macroscopic scale, the stiffness increases while the ultimate extensibility decreases. These results have been corroborated by extensive research on the effect of thermo-oxidative ageing on tensile properties of elastomers [11, 12, 13], including polychloroprene [14, 15, 16]. Authors show that the Young modulus, E, increases due to the increase in crosslink density, whereas both ultimate extension λ_b and stress σ_b decrease. Even though it has received less attention, the effect of ageing on durability such as fatigue lifetime N [17, 18, 19] and crack propagation rate [20, 21] has still been characterized, even in the case of CR [22]. With a comprehensive understanding of network changes and decline in mechanical properties, attempts have been made to establish relationships between these two factors.

An approach to establish this relationship has been proposed, based on the theory of rubber elasticity [23]. In this framework, stretch at break λ_b is expected to be related to $\nu^{-1/2}$ in uniaxial tension. This relationship has been validated for a broad range of unaged rubbers, and some studies have shown successful correlations when applied to CR ageing [15, 22]. However, there is still a need for an effective method that accurately predicts fatigue lifetime during ageing. Classically, fatigue lifetime is correlated with quasi-static properties either using the phenomenological model of Lake [17, 24] or empirical relationships involving ultimate properties [22]. This existing methodology, represented by the black arrows in Figure 1, has its limitations as ultimate properties cannot be extended to 3D problems and cannot be easily incorporated into constitutive models. Recently, there has been a rising interest in using energetic approaches to characterize fatigue change during ageing. In this context, Moon et al. [25] investigate a possible relationship between

the strain energy density and crosslinking to predict fatigue lifetime in complex blends of natural rubber and polybutadiene rubber.

In the present study, we adopt a novel strategy to directly relate fatigue lifetime to the properties of the macromolecular network during ageing. Particularly, we investigate a carbon black-filled CR that undergoes more than 25 thermo-oxidative ageing conditions. In the following, we first examine the effect of ageing on both the macromolecular network and the mechanical properties, by determining the crosslink density, the mechanical strain energy, and the fatigue lifetime of the material. Then we propose a novel approach based on the theory of rubber elasticity and that relies on the network strain energy density $W_{network}$. Using this method, represented with blue arrows in Figure 1, fatigue lifetime is satisfactorily predicted regardless of the ageing temperature for the first time on a filled elastomer.

2. Materials and methods

2.1. Material

The material is a carbon black-filled polychloroprene (15 phr), a material widely used in offshore applications. Its formulation is given in Table 1.

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
6 Phenyl-phenilenediamine	3

The material has been cured for 4 min at 177°C. It is supplied as plates of dimensions 250 mm × 250 mm × 2 mm.

2.2. Ageing method

Thermo-oxidative ageing is conducted in Memmert ovens with forced air convection, with a precision of ± 2°C. Prior to ageing, material undergoes one week of anaerobic maturation at 100°C to produce the material referred to as "unaged" in the following. Then, further exposition to air is considered as thermo-oxidative ageing. Samples are aged at room temperature (RT), 40°C, 60°C, 80°C, 90°C, 100°C, and 115°C, for various ageing durations. Oxidation is homogeneous through sample thickness.

2.3. Experiments

For each ageing condition, i.e. specific temperature and duration, swelling, quasi-static uniaxial cyclic tensile, and fatigue tests are performed. For a particular ageing condition, the results are averaged over the samples.

2.3.1. Swelling

The average crosslink density ν is determined by swelling, with a protocol essentially identical to the one of Taourit et al. [26], and based on ISO-1817 [27]. According to the Flory-Rehner theory [28], ν (in mol.cm^{-3}) is given by Equation 1.

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

where v_p is the volumic fraction of the swollen polymer, $V_{\text{tol}} = 106.3$ mL.mol^{-1} is toluene molar volume, and χ is the Flory-Huggins parameter which is commonly set to 0.4 for CR [29]. It is assumed that χ does not depend on ageing. It is to note that when calculating ν with Equation 1 for a filled rubber, it provides an apparent effective network chain density [30]. Results presented here are average crosslink densities (3 samples), measured after ageing; we do not consider any changes in ν with the fatigue test here.

2.3.2. Quasi-static uniaxial tensile tests

Samples are ISO-37 flat dumbbell specimens (H3) with dimensions specified in [31]. Tests are performed at room temperature with an Instron machine using a 10 kN load cell sensor, and a laser extensometer to measure the strain ϵ. Extension λ is defined as $\lambda = 1 + \epsilon$. The stretching rate is sufficiently low to consider the test as quasi-static: $\dot{\lambda} = 10^{-2}$ s^{-1}. For each ageing condition, samples are subjected to five cycles at a strain level of $\lambda = 2$. Three samples are tested per ageing condition and results are averaged.

2.3.3. Fatigue tests

Seven H3-samples (also detailed in [31]) are tested for each ageing condition, in "fully relaxing conditions", i.e. with a null ratio $R = 0$ between minimum and maximum applied extension. Experiments are carried out at room temperature on a specific machine visible in Figure 2 (see [32] for details). Prior to the test, the Mullins effect is eliminated as follow: samples first undergo an accommodation of 100 cycles at maximum strain, then they relax 15 min while maintaining the maximum strain.

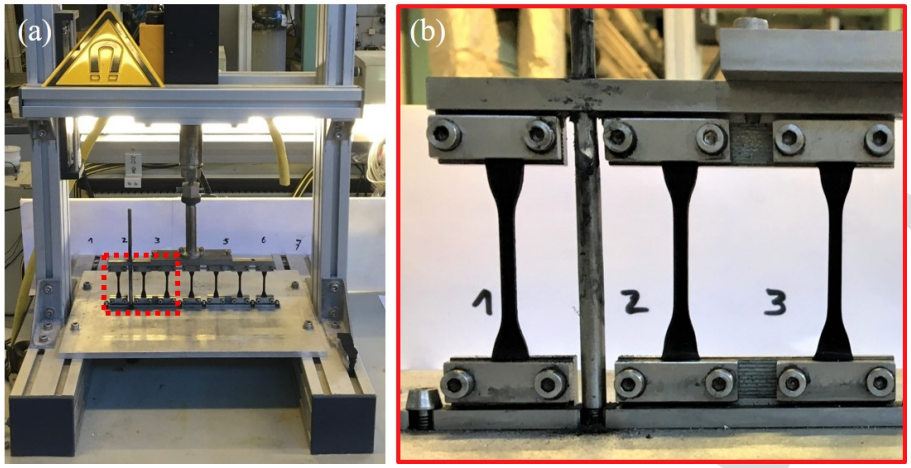

Figure 2: a) Custom-built fatigue machine featuring an electric actuator. b) Close-up view highlighting three samples

Loading conditions consist in a sine displacement at 2 Hz. During the test, pictures are recorded by a camera to determine samples break, which is considered as their end of life.

3. Results

In this section, we present the experimental results of the tests described above. The mean values of the measured parameters are presented with error bars being min/max values at a given condition.

3.1. Macromolecular network properties

The properties of the macromolecular network of the aged specimens are characterized through their average crosslink density ν. Figure 3a shows the average crosslink density of the material as a function of ageing time for a reference temperature of 80°C. Crosslink density exhibits a significant increase with ageing duration, attributed to the reaction of radicals on the double bond of the chloroprene to create new crosslinks during oxidation [6, 8, 33]. In Figure 3b, each color corresponds to a specific ageing temperature considered in this study. The material demonstrates a uniform behaviour for all temperatures, in accordance with similar studies on unfilled and filled polychloroprene [14, 15, 33]. As expected, increasing the temperature accelerates the oxidation, as illustrated by the horizontal shift between ageing temperatures. As the kinetics of CR thermo-oxidation have already been studied in previous works [9, 10], it is not investigated here. However, it is important to recall that predictions of ν can be made with kinetics models of thermo-oxidation.

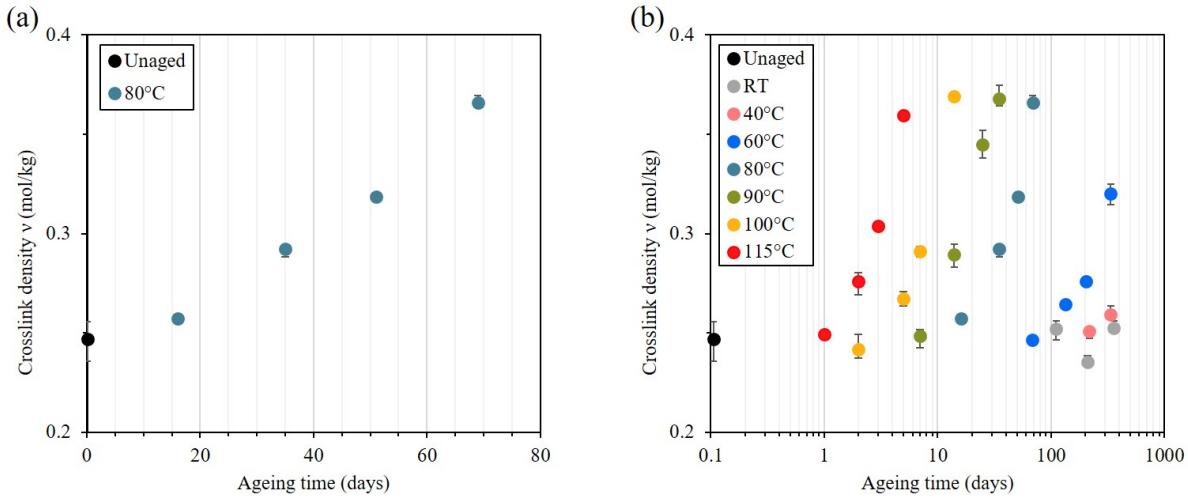

Figure 3: (a) Crosslink density ν throughout ageing time at 80°C. (b) Changes in ν for all considered ageing conditions. If not visible, deviation is within symbols width.

3.2. Quasi-static tensile properties

The tensile response of the material of the fifth cycle up to $\lambda = 2$ is presented in Figure 4a, for various ageing durations at 80°C. During ageing, we observe a stiffening that can be attributed to the increase in crosslink density measured by swelling.

Our focus heads towards the mechanical strain energy density which is calculated by integrating these stress-extension curves. This energy, referred to as W_{mech}, is calculated by Equation 2.

$$W_{mech} = \int_{\lambda=\lambda_{start}}^{\lambda=2} P(\lambda)\, d\lambda \tag{2}$$

where P is the engineering stress. Because of Mullins effect, there is permanent set when considering the fifth cycle, therefore $\lambda_{start} \geq 1$ is the first extension value for which P is positive. W_{mech} is plotted in Figure 4b for all temperatures considered. An increase in W_{mech} is observed: for example W_{mech} increases from 1.04 MJ.m^{-3} before aging, to 1.73 MJ.m^{-3} after 14 days at 100°C. It is worthnoting that this behaviour is independent of the ageing temperature. In other words, results presented in Figure 4 show that ageing temperature affects the degradation rate of CR due to thermo-oxidation but not its mechanical consequences for quasi-static loading conditions, in a qualitative manner at least. Quantitative relationship will be considered in the discussion section.

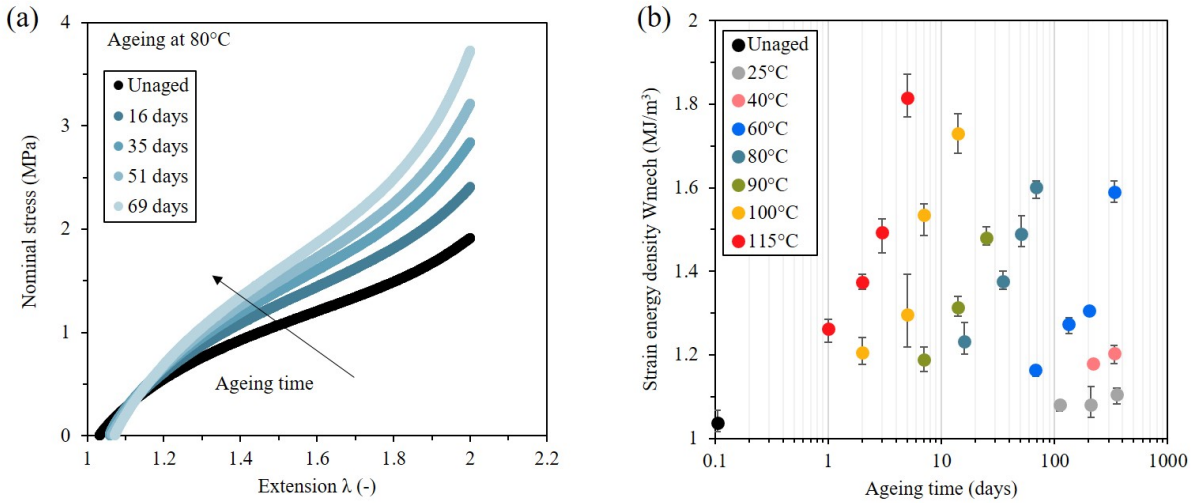

Figure 4: (a) Fifth loading paths between up to $\lambda = 2$ from cyclic tensile tests on samples aged at 80°C. (b) Increase in mechanical strain energy density with ageing time for all ageing conditions

3.3. Fatigue properties

First, the Wöhler curve of the unaged CR is constructed; it is shown in Figure 5. It depicts the maximum applied extension λ_{max} in the range of 2 to 4.5 (with $R = 0$) with respect to the number of cycles to failure N. As expected, an increase in maximal extension leads to a decrease in fatigue lifetime. As an example, when reducing λ_{max} by a factor of two (from 4 to 2), the mean fatigue lifetime is increased by a factor of 31. The fatigue lifetime of the unaged CR is consistent with previous investigations conducted on similar material formulations [22, 34, 35], although the rates of change with extension may differ.

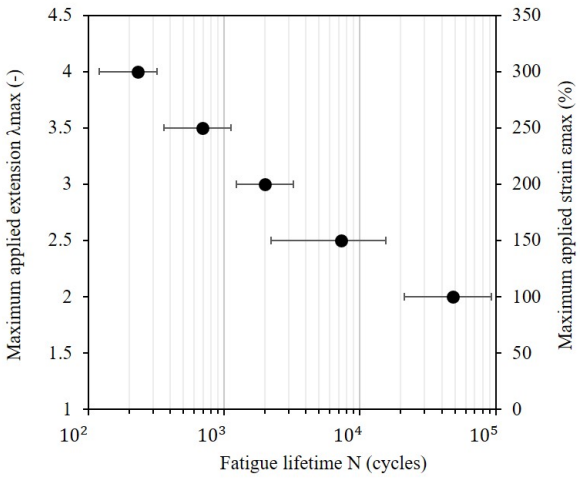

Figure 5: Wöhler curve of the unaged material

In previous investigations, research efforts have been made on crack nucleation and propagation within carbon black-filled rubber. When subjected to fatigue in relaxing conditions, the material stiffness declines gradually, mainly due to viscoelastic effects. For large number of cycles, there is a pronounced reduction in stiffness, primarily attributed to crack initiation [38]. In thin samples, complete fracture occurs rapidly after crack initiation: for this reason, some authors draw Wöhler curves for initiation specifically [39]. Observations show that cracks initiate on flaws, most frequently inclusions or carbon black agglomerates [40, 41]. Their size and volumic density rely on numerous various parameters (formulation, number of loading cycles, applied extension etc...). Two initiation mechanisms are highlighted: filler/matrix decohesion caused by agglomerates fracture, or cavitation in the vicinity of fillers or inclusions [41, 42]. In any cases, the cracks then propagate in a direction perpendicular to the loading [43].

In order to evaluate the effect of ageing on fatigue properties, fatigue tests at $\lambda_{max} = 2$ (i.e. at 100% strain) are conducted, so that variations in the fatigue lifetime with ageing are easily discernible with acceptable experimental durations. Figure 6a illustrates a significant drop in fatigue lifetime over ageing time at 80°C in air. More precisely, at this temperature fatigue half-time life is reached in less than 6 days , and fatigue lifetime decreases by a decade in 30 days. As evidenced in Figure 6b, this behaviour does not depend on the ageing temperature; only degradation rate is affected by the temperature. This is in good agreement with similar experiments previously performed on unfilled polychloroprene between 70°C and 120°C [18, 22].

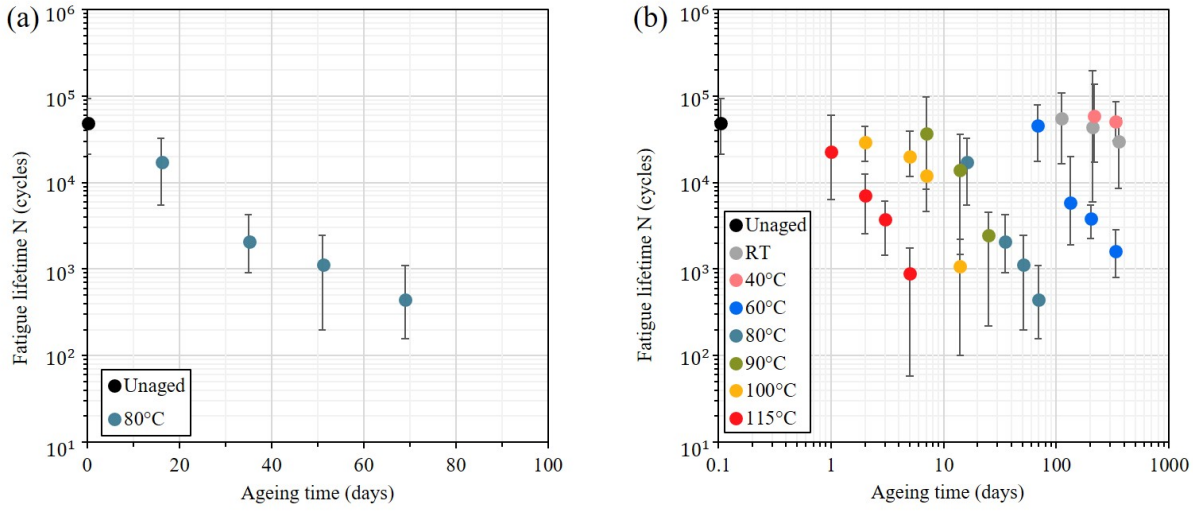

Figure 6: (a) Drop in fatigue lifetime with ageing time at 80°C. (b) Drop in fatigue lifetime for all ageing conditions.

In this section, it has been shown that thermo-oxidative ageing leads to an increase in crosslink density due to the presence of double bonds in the polymer backbone [6, 33]. This increase largely affects the mechanical behaviour of the rubber with an increase in both stiffness and mechanical strain energy, as well as a drastic decrease in fatigue properties. Finally, we have shown that the ageing temperature significantly affects the kinetics of degradation and that the impact of thermo-oxidation on the mechanical behaviour remains similar across a wide range of ageing temperatures.

Considering that the degradation of the macromolecular network can be predicted by well-established kinetic models, our next objective is to correlate ν and N in order to describe the decrease in fatigue lifetime due to this degradation.

4. Discussion

The statistical theory of rubber elasticity and its extensions relate the mechanical response of the material to the characteristics of its macromolecular network through the strain density energy (see for example Treloar 1975 [23]). However, such approach has not been previously explored to explain the decrease in fatigue life of carbon black-filled elastomers during degradation. Assuming that the crosslink density can be successfully predicted using existing kinetics models [9, 10, 36], a two-step approach is proposed here:

- First, we define a "network strain energy density" based on existing theory and verify its consistency with our experimental data.
- Second, we establish a relationship between this network strain energy and fatigue properties.

4.1. Network and mechanical experimental strain energy density

The assumptions adopted for the classical statistical theory of rubber elasticity are [23, 44] :

- A macromolecular chain is defined as a segment of molecule between successive points of cross-linkage.
- The mean-square end-to-end distance of the unstrained assembly of chains is the same as for a corresponding set of free chains.
- There is no change of volume on deformation.
- The network follows an affine model [37].
- The chains are Gaussian : network entropy is the sum of all individual chains entropies.

Following the latter hypothesis, it is possible to derive the total entropy of deformation and to establish the expression of the Helmoltz free energy, by assuming internal energy remains constant during deformation. Finally, it leads to Equation 3, where $W_{network}$ is the work of deformation at constant volume, i.e. the elastically stored free energy per unit volume of the rubber.

$$W_{\text{network}}(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}\rho RT\nu \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right) \tag{3}$$

where ρ is the material density, R is the molar gas constant (R = 8.31 J.mol^{-1}.K^{-1}), T the temperature (in K), ν the crosslink density (in mol.cm^{-3}), and $\lambda_1, \lambda_2, \lambda_3$ the stretch ratios in principal directions. In simple extension, one dimension of the samples is increased by $\lambda_1 = \lambda$, whereas the two other dimensions are reduced correspondingly with the incompressibility condition : $\lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}$. Hence, the according strain energy density is now given by Equation 4:

$$W_{\text{network}}(\lambda) = \frac{1}{2}\rho RT\nu \left(\lambda^2 + \frac{2}{\lambda} - 3\right) \tag{4}$$

Here, the CR is filled by 15 phr of carbon black, and the expression of $W_{network}$ takes into account the presence of fillers as a function of the effective crosslink density ν. However, the validity of this description needs to be verified. As mentioned above, it is possible to measure the mechanical strain energy $W_{mech}(\lambda)$ by integrating the quasi-static cyclic tensile test curves shown in Figure 4a. Therefore, by considering the energy stored at $\lambda = 2$, we can compare W_{mech} obtained in Section 3.2 with the expression of $W_{network}$ in Equation 5:

$$W_{\text{network}}(\lambda = 2) = \rho RT\nu \tag{5}$$

Figure 7 illustrates the correlation between $W_{network}$ and W_{mech} for all ageing conditions. The increase in $W_{network}$ signifies crosslinking, which in turn leads to the stiffening of the material. As a result, there is an elevation in W_{mech}, indicating a higher amount of mechanical strain energy stored in the material. Quantitatively, a linear correlation between strain energies is observed, with a slope close to one. This suggests that the energy required to stretch a sample up to $\lambda = 2$ closely matches the stored free energy predicted by Treloar's theory, demonstrating the relevance of the approach proposed here. As a result, thanks to Figure 7, for a given ν, it is possible to predict quasi-static energy density W_{mech} at $\lambda = 2$ independently of the ageing condition. This validates the use of $W_{network}$ as an indicator of network degradation.

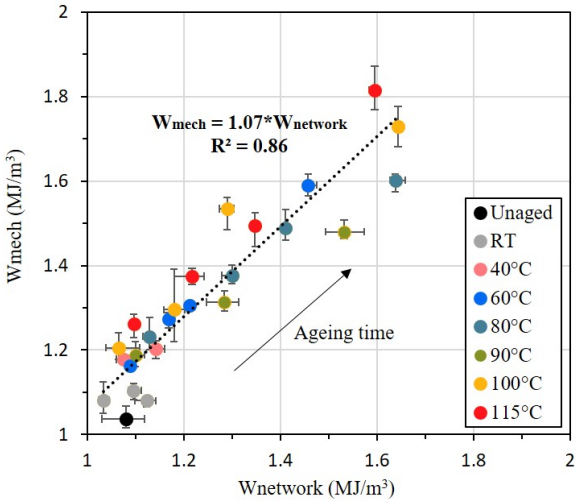

Figure 7: Correlation between measured strain energy density W_{mech} and theoretical $W_{network}$ for all ageing conditions

4.2. Correlation between fatigue lifetime and network strain energy density

Let us now investigate the potential relationship between fatigue lifetime N and $W_{network}$. Figure 8 illustrates the according correlation for all ageing conditions. For samples with small values of $W_{network}$, corresponding to unaged and slightly aged samples, the mean fatigue lifetime is concentrated around 30 000 and 60 000 cycles. As ageing becomes more severe, $W_{network}$ increases because of crosslinking and fatigue lifetime decreases accordingly. The y-axis being logarithmic, the decrease in N with $W_{network}$ is exponential and does not depend on ageing temperature. These findings demonstrate that network strain energy density is a reliable predictor of fatigue lifetime during thermo-oxidative ageing. It is important to note that the methodology outlined in this paper does not currently incorporate variations in crosslinking density during fatigue testing performed at room temperature. This aspect will need to be studied in the future to consider the potential coupling between elastomer fatigue and aging.

In previous studies, empirical relationships involving stretch at break λ_b and fatigue lifetime N have been proposed (see Figure 1) and they often provide acceptable correlations [22]. However, when these approaches are extended to structural analysis, concerns arise due to the difficulty of incorporating stretch at break into constitutive equations of elastomers, making the corresponding finite element implementation challenging. Moreover, λ_b loses its relevance when dealing with multiaxial deformation. Since the strain energy density naturally extends from uniaxial to three-dimensional formulation, the proposed approach addresses this limitation and offers potential for applications in structural analysis. In future investigations, the consistency

of our approach should be studied for other fatigue loading ratios ($R \neq 0$) and larger strain ($\lambda > 2$).

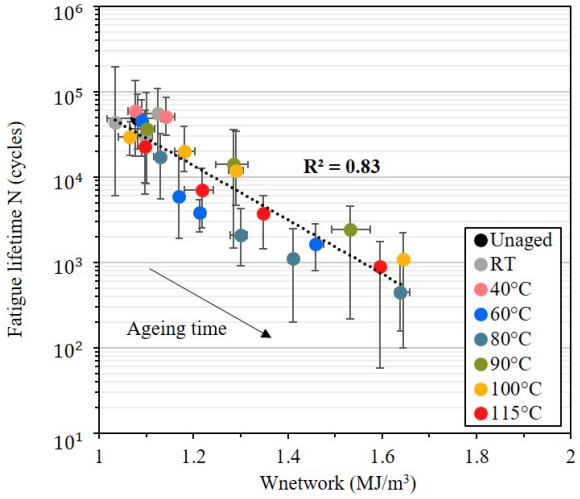

Figure 8: Relationship between fatigue lifetime N and strain energy density $W_{network}$ for all ageing conditions

5. Conclusions

In the present work, thermo-oxidative ageing of carbon black-filled polychloroprene rubber has been thoroughly investigated and a significant effort has been made to relate fatigue properties to changes in the macromolecular network. As established in former studies, oxidation induces an increase in CR network crosslinking due to radical reactions on the polymer backbone. This results in a significant stiffening of the material which manifests by an increase in mechanical strain energy density at the macroscopic scale. In terms of fatigue properties, we have observed an exponential decline in fatigue lifetime. Moreover, we have found that this behaviour is independent of temperature, suggesting that temperature primarily influences the kinetics of the degradation process.

The major finding of the present study is that the network strain energy density $W_{network}$, derived thanks to the statistical theory of rubber elasticity, agrees very well with experimental fatigue results for filled CR throughout ageing. This physical quantity is revealed as a reliable predictor of fatigue properties without relying on fracture properties as an intermediary. However, further experiments will be necessary to validate the approach for a broader range of mechanical loadings. In particular, non-relaxing fatigue ratios ($R > 0$), and larger strain ($\lambda > 2$) should be investigated.

CRediT authorship contribution statement

Hugo Madeira: Conceptualization, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing.

Pierre-Yves Le Gac: Conceptualization, Formal analysis, Writing – Review & Editing, Supervision.

Maelenn Le Gall: Conceptualization, Formal analysis, Writing – Review & Editing, Supervision.

Erwan Verron: Conceptualization, Formal analysis, Writing – Review & Editing, Supervision.

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.

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Highlights:

- Thermo-oxidative ageing of a carbon black-filled polychloroprene is investigated
- Ageing causes network crosslinking and drop in quasi-static and fatigue properties
- Experimental strain energy density matches the theory of rubber elasticity
- Network strain energy predicts fatigue lifetime independently of the temperature

CRediT authorship contribution statement

Hugo Madeira: Conceptualization, Formal analysis, Investigation, Writing - Original Draft, Writing – Review & Editing.

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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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: