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## Impact Of Carbon Black Content In Relationships Between Mechanical Properties And Crosslinking Of Filled Polychloroprene During Oxidative Aging

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### Abstract :

Carbon black (CB) fillers are widely used in elastomer compounds to improve their mechanical performance. Extensive studies conducted over more than 80 yr now have provided a satisfactory understanding of the influence of CB content on the mechanical properties of elastomers. However, in the majority of the studies devoted to aging, similar elastomer formulations with different CB contents are often considered as independent materials, which hinders the applicability of structure–property relationships. Herein, we reconcile the effects of aging and CB content by investigating the oxidative aging at 80 °C in air of a polychloroprene rubber with four different CB contents (from 10 to 45 parts per hundred of rubber). Both macromolecular network and mechanical properties are determined via swelling, uniaxial tensile, and fatigue tests. It is shown that the response of the materials can be decomposed into the contributions of elastomer matrix and fillers. The behavior of the matrix during aging is the same regardless of the CB content. Relationships between the microstructural characteristics of the matrix and the local mechanical properties are then derived. Their relevance for aged materials and for a wide range of CB content are demonstrated.

- Oxidative ageing is performed on polychloroprene at different carbon black contents.
- The apparent crosslink density is related to the one of the unfilled rubber matrix.
- Crosslinking of the matrix behaves the same independently of fillers content.
- Mechanical properties are linked to the matrix network through ageing.
- At moderate contents, fillers effect follows established reinforcement theories.

# 1. Introduction

Carbon black (CB) particles have been used in rubber compounding since the beginning of the 20<sup>th</sup> century. Adding CB to rubber compounds leads to substantial changes in mechanical properties, enabling manufacturers to improve the performance of their products [1]. Motivated by industrial requirements, research works on CB effects emerged with Guth's theory of reinforcement [2]. Since then, numerous experimental works have been carried out on filled elastomers, progressively unravelling the dependence on CB content of their mechanical response under quasi-static loading conditions. The microscopic interaction of filler particles with the elastomer matrix received a particular focus [3] [4]. Filler-reinforcement, which was initially modelled for limited CB contents, is now partly understood for moderately filled formulations through the concept of bound rubber [5] [6]. Recently, the effect of CB content has been closely inspected on other mechanical characteristics, such as hysteresis [7], fatigue life [8], and strain induced crystallization [9].

Alongside these advances, the durability of rubber during ageing has attracted much attention. The first studies on oxidative ageing of rubbers date back to the 1960s. Degradation mechanisms and their kinetics were studied, initially without considering CB reinforcement [10]. Extending such investigations to filled materials complicates the understanding, and studies devoted to the effect of CB content on oxidation remain rare and mainly focused on chemistry. Their results are complex: CB particles can act as catalysts or inhibitors, depending on the elastomer matrix, temperature, environment, and specific surface area of the fillers, among others [11] [12]. However, this puzzling issue has been mitigated by considering each rubber matrix with a given carbon black content as a different material from the same matrix with another content, i.e. the effect of ageing is studied on *a priori* independent materials of similar formulations, rather than a [rubber matrix + fillers] composite material. With this approach, the implications of ageing on the microstructure of elastomers have been studied: during oxidation, elastomer networks can undergo chain scission or additional crosslinking, which modify the length of elastically active chains [13] [14]. These microstructural changes have a major influence on the macroscopic properties of rubbers [15] [16], and typically lead to a drop of performance.

The description and prediction of this decrease in performance has been extensively studied in recent years, particularly with regards to mechanical properties such as tensile strength [17] and fatigue life [18] [19]. A convenient approach is to derive structure-properties relationships by linking the mechanical properties directly to the characteristics of the macromolecular network. For example, Lake proposed a linear relationship between the crosslink density of the network,  $\nu^{-1/2}$ , and the strain at break  $\lambda_b$  for unfilled rubbers, within the context of rubber elasticity [20]. This relationship has subsequently been verified for numerous other elastomers [21], including carbon black-filled materials [22]. Other empirical relations between cyclic or fatigue properties and the network characteristics have also been proposed [23], [24]. However, the crosslinking density measured by swelling not only takes into account the behaviour of the polymer network, but also the interactions between chains and fillers. As a consequence, the relationships between mechanical properties and  $\nu$  for filled rubbers cannot be established without corrective factors.

In the present work, thermo-oxidative ageing is carried out on a polychloroprene rubber with four contents of carbon black. The effects of both CB content and ageing on macromolecular network and mechanical properties are examined by determining the crosslink density, tensile properties and fatigue life of the materials. Then, by considering each material as a mix of an unfilled rubber matrix and CB fillers, relationships between network and the mechanical properties are established. This renders possible to apply the results obtained in durability studies of a given elastomer to its counterparts with a different CB content.

## 2. Materials and methods

### 2.1. Materials

The investigations are performed on a carbon-black filled polychloroprene (CR), with four CB contents: 10, 15, 30 and 45 phr (in mass) of carbon black HAF N330. Table 1 presents the exact formulations, densities and volume fractions of CB. All materials were cured 10 min at 170°C and are supplied as 250 x 250 x 2 mm<sup>3</sup> sheets.

### 2.2. Ageing method

Thermo-oxidative ageing is carried out in Memmert ovens, with forced air convection, with an accuracy of  $\pm 2^\circ\text{C}$ . Similarly than in [19], prior to ageing, the materials undergo one week of anaerobic maturation at 100°C, to produce the material referred to as “unaged” in the following. For each CB content, samples are aged for four durations (16, 35, 50 and 69 days) at 80°C. At this temperature, it has been verified that oxidation is homogeneous through the thickness of samples [25].

Table 1: Materials formulation and some physical properties

| Material designation       | CB10      | CB15      | CB30      | CB45      |
|----------------------------|-----------|-----------|-----------|-----------|
| <b>Formulation</b>         |           |           |           |           |
| Polychloroprene type W     | 100       | 100       | 100       | 100       |
| Carbon black HAF N330      | <b>10</b> | <b>15</b> | <b>30</b> | <b>45</b> |
| Sulfur                     | 1.875     | 1.875     | 1.875     | 1.875     |
| MgO                        | 4         | 4         | 4         | 4         |
| ZnO                        | 5         | 5         | 5         | 5         |
| Stearic acid               | 0.5       | 0.5       | 0.5       | 0.5       |
| <b>Physical properties</b> |           |           |           |           |
| Density (-)                | 1.336     | 1.351     | 1.374     | 1.408     |
| Volume fraction of CB (-)  | 0.056     | 0.082     | 0.150     | 0.208     |

## 2.3. Experiments

Swelling, uniaxial tensile and fatigue tests are performed for each material at each ageing condition. Experimental protocols being essentially similar to those in [19], only the fundamentals are recalled in this section.

### 2.3.1. Swelling tests

The average crosslink density of the materials  $v_{app}$  is determined by swelling tests of CR offcuts, in accordance with ISO-1817 [26]. The Flory-Rehner theory gives [27]

$$v_{app} = -\frac{1}{V_{tol}} \frac{[\ln(1 - v_{p,app}) + v_{p,app} + \chi v_{p,app}^2]}{v_{p,app}^{\frac{1}{3}} - \frac{v_{p,app}}{2}},$$

Equation 1

where  $v_{p,app}$  is the volume fraction of the swollen [polymer + fillers] composite,  $V_{tol} = 106.3$  mL/mol is the molar volume of toluene, and finally  $\chi$  is the Flory–Huggins parameter which is commonly set to 0.4 for CR [28] (here, it is considered independent of ageing). It is to note that  $v_{app}$  is an apparent crosslink density, which encompasses both intramolecular crosslinks and filler/matrix linkages [29].

Three samples are tested per material and ageing duration. As the corresponding results are reproducible, they are averaged.

### 2.3.2. Uniaxial tensile tests

Uniaxial tensile tests are performed on ISO-37 H3 flat dumbbell specimens, the dimensions of which are given in the corresponding standard [30]. The tests are carried out at room temperature, on a INSTRON 5966 testing machine, equipped with a 10 kN load cell and a laser extensometer prescribing deformation  $\varepsilon$  (in %). The according strain  $\lambda$  is  $1 + \varepsilon$ , and the strain rate is  $\dot{\lambda} = 10^{-2} \text{ s}^{-1}$ , which is low enough to consider the tests as quasi-static. Again, three samples are tested per material and ageing condition, and results are averaged.

Among available data, strain at break  $\lambda_b$  directly measured by the extensometer, is of particular interest. Moreover, the modulus  $E$  is determined by

$$E = 6 \times (C_1 + C_2),$$

Equation 2

where  $C_1$  and  $C_2$  are the Mooney-Rivlin model parameters, obtained by fitting the experimental nominal stress (Piola-Kirchhoff I) as a function of  $\lambda$  for small strain, i.e.  $\lambda \in [1; 1.2]$ .

$$P = 2 \left( C_1 + \frac{C_2}{\lambda} \right) \left( \lambda - \frac{1}{\lambda^2} \right).$$

Equation 3

### 2.3.3. Fatigue tests

To address the large deviation in measurements of elastomer fatigue life, seven ISO-37 H3 samples are tested for each material at each ageing condition. The experimental set-up involves a custom-built machine with controlled displacement (for details, see [31]). The tests are performed at room temperature, and only fully relaxing conditions are considered; the loading ratio between minimum and maximum prescribed displacement is  $R = 0$ . Before testing a sample, a preliminary accommodation of 100 cycles at maximum strain followed by 15 min of relaxation at maximum strain is operated, so that the Mullins effect fades away. The loading displacement signal is sinusoidal at a frequency of 2 Hz. The end-of-life criterion consists of the complete failure of the specimen; it is determined by the acquisition of images during the test.

## 3. Results

This section presents the results of the aforementioned experiments, starting with the properties of the unaged materials. Then, the effect of ageing on the elastomer network and mechanical properties is presented.

### 3.1. Unaged materials

#### 3.1.1. Macromolecular network

Figure 1 shows the apparent crosslink density of the filled materials  $\nu_{app}$  (in mol/L) obtained by swelling, as a function of the CB content. It is observed that the crosslink density increases as fillers are added within the matrix.

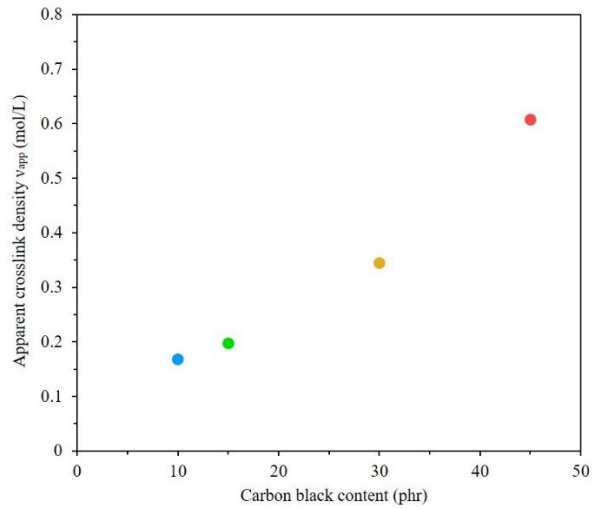


Figure 1: Impact of CB content on apparent crosslink density  $\nu_{app}$ , in the unaged state

#### 3.1.2. Tensile behaviour

The nominal stress-strain curves of the unaged materials are plotted in Figure 2. As the CB content increases, the stiffness increases and the maximum strain that the material can sustain decreases. Figure 3 presents the modulus  $E$  (Equation 2) and the strain at break  $\lambda_b$  as a function of CB content.

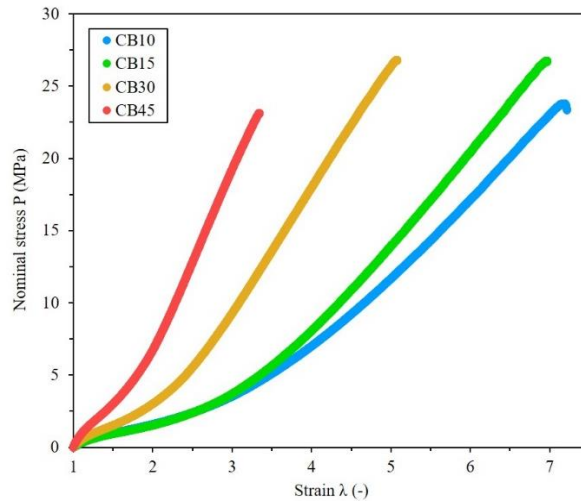


Figure 2: Influence of the CB content on the uniaxial tensile response of the unaged materials

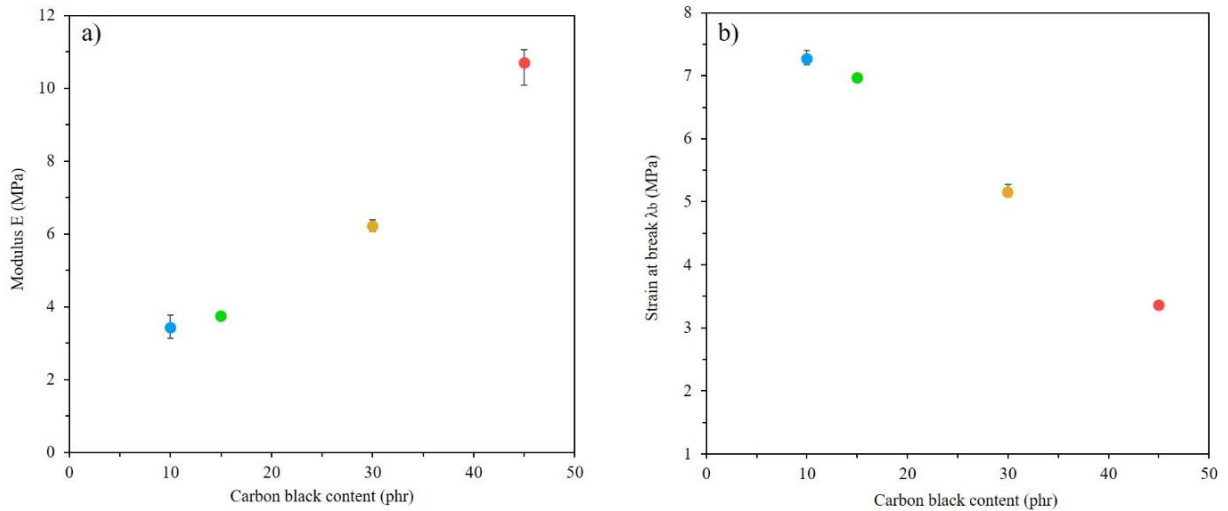


Figure 3: Influence of the CB content on (a) the modulus and (b) the strain at break of the unaged materials

### 3.1.3. Fatigue life

The fatigue properties are measured with a loading ratio  $R=0$  and at various prescribed strain  $\lambda$  between 2 and 3.5. The mean fatigue life, i.e. number of cycles to failure, is plotted as a function of CB content in Figure 4; error bars indicate minimum and maximum values. The same behaviour is observed regardless the applied strain: adding fillers to the polychloroprene matrix appears to enhance fatigue life up to a certain CB content, above which a drop occurs. It should be noted that, as observed in many other studies on polychloroprene fatigue [32] [24], deviation is large. In the following, fatigue is considered only at  $\lambda=2$ , so that variations of lifetimes are easily discernible within reasonable experimental durations.

The effect of carbon black content on the network and mechanical properties has been analysed for unaged materials. Our attention now shifts towards the effect of ageing.

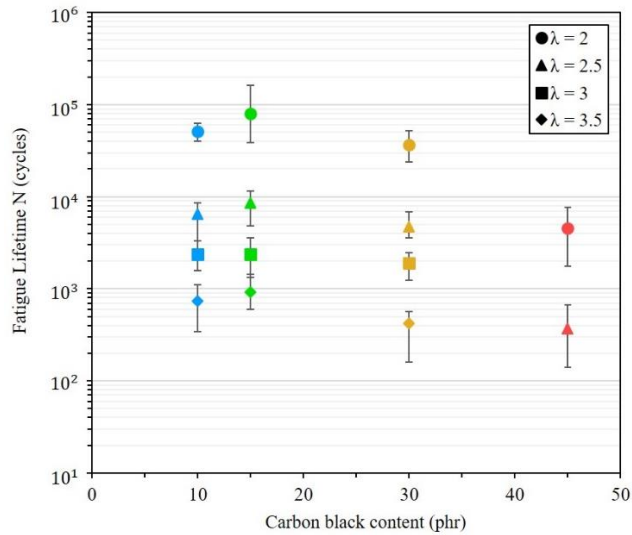


Figure 4: Influence of CB content on fatigue life for the unaged materials

### 3.2. Effect of ageing

This section presents the results for aged materials. For each CB content and the four ageing conditions, the same experiments are carried out as for the unaged materials.

#### 3.2.1. Macromolecular network

The change in effective crosslink density  $v_{app}$  with ageing time is shown in Figure 5. It appears clearly that thermo-oxidative ageing induces an increase in  $v_{app}$ , regardless the CB content. This increase has been observed many times for CR [33] [34], including by the present authors on a similar formulation [19]. It can be attributed to the main degradation mechanism of polychloroprene during thermo-oxidative ageing: radicals react on the alkene bonds to create new crosslinks [35] [36].

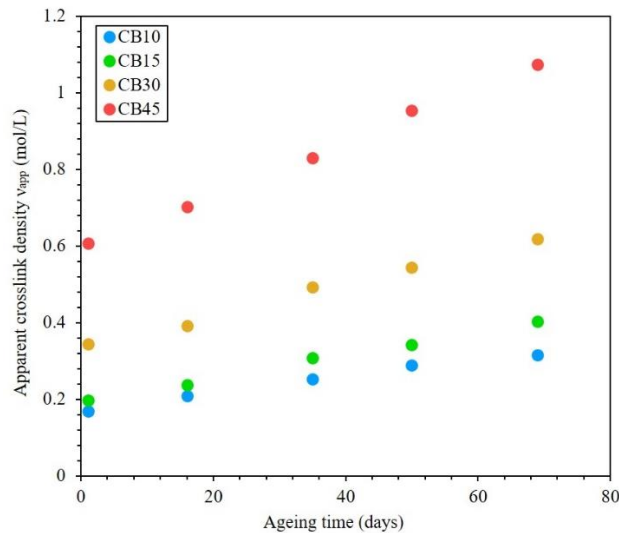


Figure 5: Effect of thermo-oxidation at 80°C on apparent crosslink density  $v_{app}$  for different CB contents

#### 3.2.2. Tensile behaviour

The effect of ageing on the tensile properties is illustrated in Figure 6, where the stress-strain curves of CB10 are plotted at each ageing duration. For this given CB content, the material undergoes a remarkable stiffening during ageing, as well as a decrease in strain at break. This concurs with the

reduction in extensibility attributed to the increase in  $v_{app}$ . Let us now consider all the formulations, by examining the evolution of both modulus  $E$  and strain at break  $\lambda_b$  during ageing, as depicted in Figure 7. The effect of ageing on the mechanical properties is independent on CB content: the material stiffens when exposed at  $80^\circ\text{C}$ , while its ability to undergo large strain decreases.

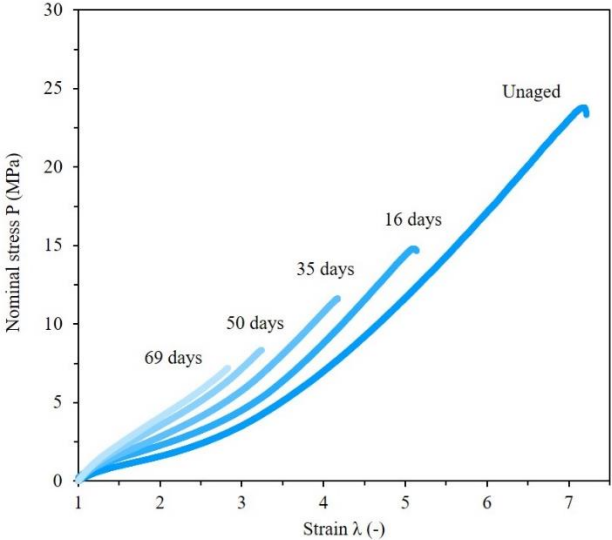


Figure 6: Effect of thermo-oxidation at  $80^\circ\text{C}$  on the tensile behaviour of the CB10 material

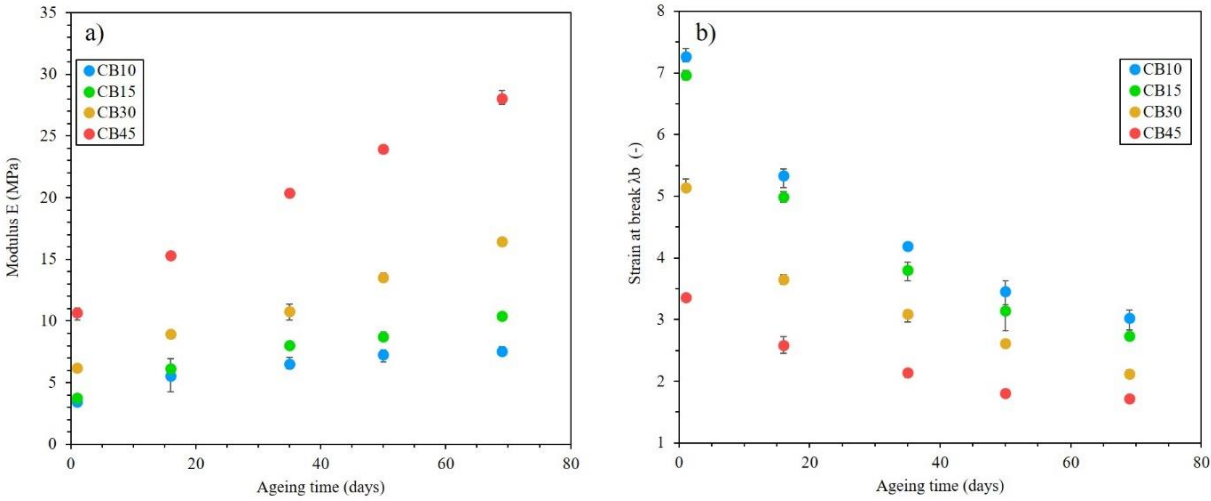


Figure 7: Effect of thermo-oxidation at  $80^\circ\text{C}$  on (a) modulus and (b) strain at break for different CB contents

### 3.2.3. Fatigue life

The fatigue lives for all the formulations tested at  $\lambda=2$  in fully relaxing conditions ( $R=0$ ) are presented in Figure 8, as a function of ageing time. A drastic drop in fatigue life is observed, with similar trends for CB10, CB15 and CB30. The CB45 material undergoes a similar drop, but due to its lower unaged fatigue life, the material breaks after a few cycles after 35 days at  $80^\circ\text{C}$  (in agreement with  $\lambda_b$  in Figure 7). Despite large error bars that complicate the analysis, the overall effect of ageing on fatigue life under these conditions appears to be independent of the CB content.

After experiments on both unaged and aged materials, our observations can be summarised as follows.

- (i) CB content has a significant impact on the mechanical properties of unaged and aged materials;

- (ii) Ageing leads to the same evolution trends of mechanical properties, whatever the CB content.

Our objective is now to develop relationships between these properties and the characteristics of the macromolecular network, in an effort to describe the decline of mechanical properties through ageing independently of their CB content.

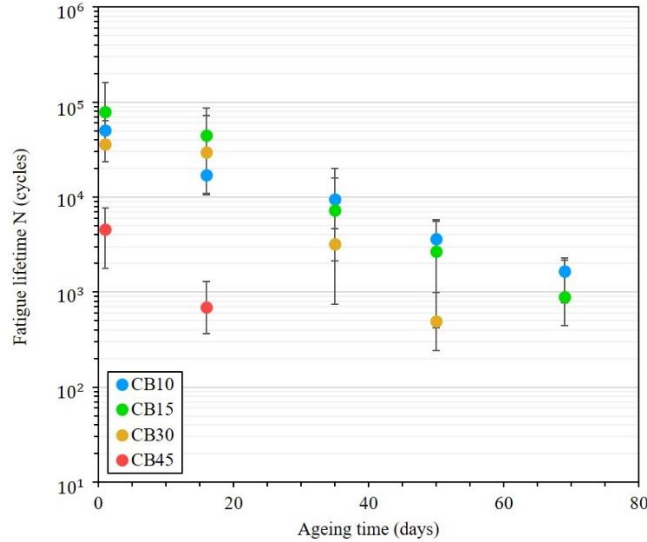


Figure 8: Effect of thermo-oxidation at 80°C on fatigue life at  $\lambda=2$  for different CB contents

## 4. Discussion

As pointed out above, the crosslink density  $v_{app}$  is referred to as apparent: it encompasses both intramolecular crosslinks and rubber-filler interactions. In this section, we first examine whether it is possible to decompose  $v_{app}$  into contributions of the matrix crosslink density  $v_{matrix}$  and of fillers. Next, we investigate how the change in mechanical properties during ageing can be predicted from  $v_{matrix}$  and the CB content.

### 4.1. Effect of thermo-oxidation on filled network

Here, we adopt Kraus interpretation of the swelling of filled elastomers [37]; it is based on the following assumptions

- (i) Fillers are spherical particles that do not swell.
- (ii) Fillers prevent swelling by adhesion: rubber chains in contact with surface of fillers do not swell. These chains are often referred to as “bound rubber”.
- (iii) Fillers induce a swelling deficiency in rubber due to adhesion. This deficiency varies continuously with distance from the filler surface, and becomes zero (swelling equal to that of unfilled rubber) far away from the filler surface.
- (iv) Filler particles are sufficiently dispersed: they do not interact with each other.

With these assumptions, the apparent volume fraction of the elastomer  $v_{p,app}$  in the swollen state can be related to the one of the rubber matrix,

$$\frac{v_{p,matrix}}{v_{p,app}} = 1 - \frac{c}{(1-c)} \left[ 3C (1 - v_{p,matrix})^{\frac{1}{3}} + v_{p,matrix} - 1 \right],$$

Equation 4

where  $v_{p,matrix}$  is the volume fraction of the unfilled rubber matrix,  $c$  is the volume fraction of CB, and  $C$  is a parameter of the order of unity that describes how the swelling deficiency decreases with the distance from the filler surface.

With the measurements of  $v_{p,app}$  at different CB volume fractions  $c$ ,  $v_{p,matrix}$  and  $C$  are easily identified by fitting  $1/v_{p,app}$  as a function of  $c/(1-c)$ , as shown in Figure 9. Then, the crosslink density of the unfilled rubber matrix  $v_{matrix}$  can be calculated with Equation 1. The corresponding values are  $v_{matrix} = 0.131 \text{ mol/L}$  and  $C = 0.92$ . Thus, the microstructure of the materials can be described by the crosslink density of the CR rubber matrix,  $v_{matrix}$ , and the CB volume fraction.

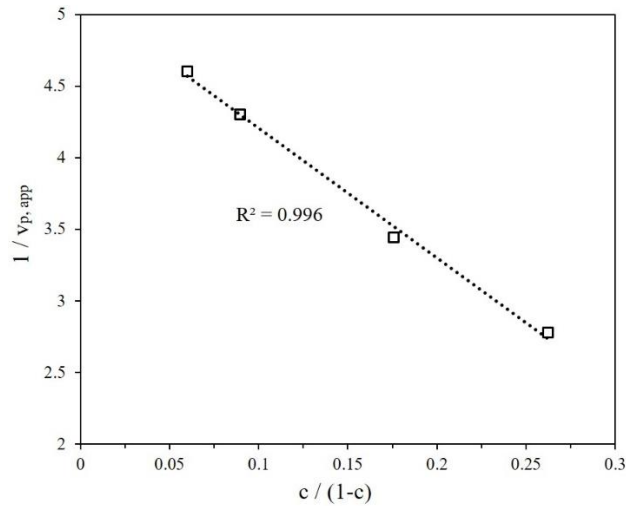


Figure 9: Fit of the parameters  $C$  and  $v_{p,matrix}$

Assuming that  $C$  does not change with ageing, it is then possible to calculate the change in  $v_{matrix}$  during thermo-oxidation using Eq. (4) and (1). Its evolution with ageing time at  $80^\circ\text{C}$  for different CB contents is shown in Figure 10. It can be seen that the increase in  $v_{matrix}$  with ageing time is similar for CB contents of 10, 15 and 30 phr, suggesting that matrix crosslinking can take place independently of filler content. This results highlights that CB does not change the crosslinking in CR during oxidation when the CB amount is below 30 phr. The slower increase observed for the 45 phr filled rubber can be attributed to the inapplicability of Equation 4 for high CB volume fractions, because assumption (iv) is no longer fulfilled.

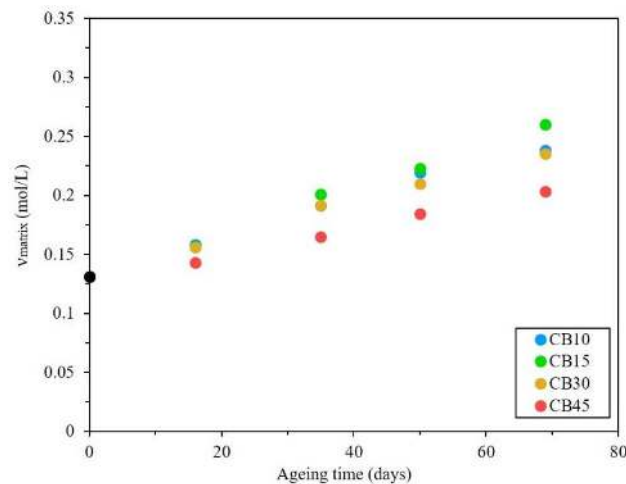


Figure 10: Evolution of the crosslink density of the matrix with ageing time

## 4.2. Relationship between network and mechanical properties during ageing

So far, we have demonstrated that the macromolecular network characteristics of our materials can be determined by separating the contributions from the unfilled rubber matrix and the fillers. In order to relate the mechanical properties and those of the network, we consider that the change in macromolecular structure due to ageing is solely due to the crosslinking of the rubber matrix, irrespective of the carbon black content. In the following, we attempt to integrate the effect of CB content into the relationships between network and mechanical properties.

### 4.2.1. Modulus

First, the statistical theory of rubber elasticity in unfilled rubber provides the following relationship between the modulus  $E_{\text{matrix}}$  and  $v_{\text{matrix}}$  [4]

$$E_{\text{matrix}} = 3\rho RTv_{\text{matrix}},$$

*Equation 5*

where  $\rho$  is the material density,  $R$  is the molar gas constant ( $R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), and  $T$  is the absolute temperature. Second, the theory of filler reinforcement modifies this equation for filled rubbers

$$E(c) = E_{\text{matrix}} \times f(c),$$

*Equation 6*

where  $f$  is a function of filler content  $c$ . This model has first been established by Guth & Gold [2], with a function

$$f_{\text{GG}}(c) = 1 + 2.5c + 14.1 c^2.$$

*Equation 7*

However, this equation is based on the assumption of perfect dispersion of the fillers, i.e. assumption (iv) in Section 4.1. In practice, this assumption is no longer valid when  $c$  exceeds 0.1; research efforts have been made to extend the approach to higher CB contents [5] [6].

The recent approach proposed by Fukahori et al. [38] considers that CB particles are connected together by bound rubber, which extends the upper limit of  $c$  to 0.3. Instead of the volume fraction  $c$ , the authors introduce an effective volume fraction  $c_{\text{eff}} = p \times c$ , where  $p$  is a parameter that empirically quantifies the thickness of the bound rubber layer and depends on the nature of fillers. In addition, the significant increase in stiffness of highly filled rubbers justifies the introduction of a third power of  $c_{\text{eff}}$  to propose a new estimate function

$$f_{\text{FUKA}}(c_{\text{eff}}) = 1 + 2.5 c_{\text{eff}} + 14.1 c_{\text{eff}}^2 + k \times c_{\text{eff}}^3,$$

*Equation 8*

in which  $k$  is a parameter that accounts for the filler surface area. In our case, fillers are high abrasion furnace (HAF) N330 which corresponds to the following parameters:  $p=1.46$  and  $k=60$  [38]. According  $c_{\text{eff}}$  values are given in Table 2.

*Table 2: Equivalence between CB content, volume fraction and effective volume fraction*

| CB content (phr) | Volume fraction $c$ (-) | Effective volume fraction $c_{\text{eff}}$ (-) |
|------------------|-------------------------|--|
| 10               | 0.056                   | 0.082  |
| 15               | 0.082                   | 0.120  |
| 30               | 0.150                   | 0.218  |
| 45               | 0.208                   | 0.303  |

From Eq. 5 and 6, it means that the modulus  $E$  of a filled rubber plotted against  $v_{\text{matrix}} \times f(c)$  should result in a straight line of slope  $3\rho RT = 9.9$ . Figure 11 enables this comparison, by plotting modulus  $E_{\text{measured}}$  (identified from tensile tests) on the y-axis against  $v_{\text{matrix}}$ , considering either the Guth and Gold (a) or the Fukahori correction (b), on the x-axis.

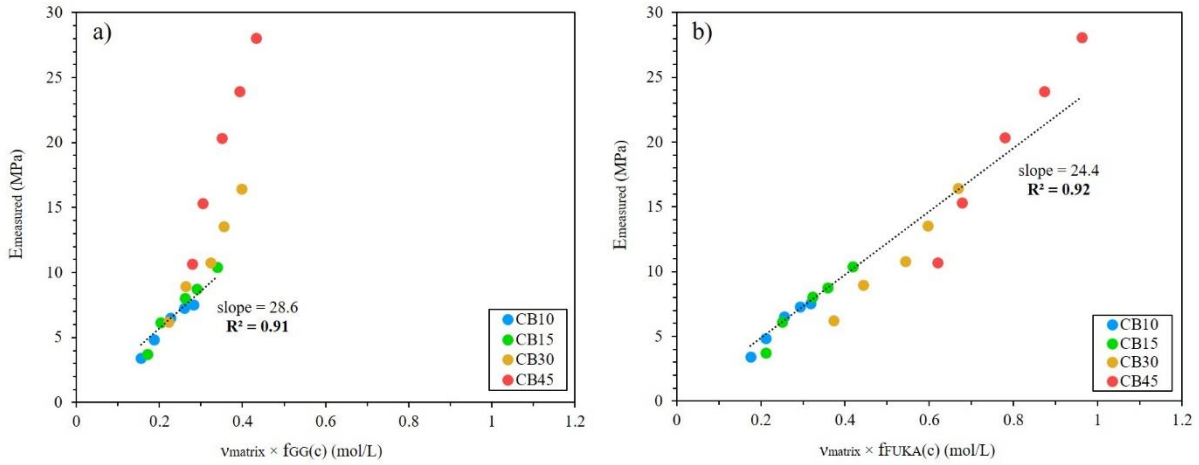


Figure 11: Prediction of the modulus by (a) the Guth and Gold model, (b) the Fukahori model

Both models qualitatively predict the effect of reinforcement in their respective application areas. Guth and Gold model remarkably unifies the data for CB10 and CB15 (see Fig. 11(a)); however data for CB30 and CB45 cannot be reproduced by the model because the actual filler volume fraction is outside its range of applicability, i.e. for CB30 and CB45,  $c > 0.1$ . As shown in Fig. 11(b), the Fukahori model unifies all the data with a remarkable correlation factor. This demonstrates that the extension to higher filler contents is relevant, even if it requires to take into account the nature of the carbon black fillers through the  $p$  and  $k$  parameters. Hence, the qualitative evolution of the modulus with ageing time is well-captured by both models in their respective range of applicability. However, from a quantitative point of view, both models underestimate the measured modulus  $E_{\text{measured}}$  obtained from  $v_{\text{matrix}} \times f(c)$ . In fact, the slopes values are substantially greater than the theoretical value predicted by the theory of rubber elasticity, by a factor 2.9 for Guth and Gold and 2.5 for Fukahori. Similar deviations from an ideal network have already been observed, in proportions very alike to those [39]. These deviations can be attributed to network imperfections when considering a non-ideal rubber, particularly the presence of entanglements and chain-ends [40], or heterogeneities in crosslink density. In future endeavours, these imperfections may be revealed thanks to double quantum nuclear magnetic resonance (DQ-NMR) [41] [42].

#### 4.2.2. Strain at break

When the study is extended to large strain, the previous relationships are not applicable. This section aims to describe changes in maximal strain at break of polychloroprene rubber with different CB contents, based on physical considerations. To do so, the concept of local strain  $\Delta$  must be introduced here: it is the strain experienced by individual rubber chains within the material, highly influenced by the presence of carbon black particles. In other words, at the microscopic scale, CB fillers locally amplify strains due to the occluded rubber, resulting in discrepancies between the local strain  $\Delta$  of the elastomer matrix and the macroscopic strain  $\lambda$ . This is the origin of the reinforcing effect of fillers, which depends on the amount, type and size of CB. Furthermore, it explains why strain at break  $\lambda_b$  decreases when the amount of CB increases for unaged materials, as shown in Figure 3b. To take into account this phenomenon, we consider the strain amplification factor  $\alpha$  [43]:

$$\Delta(c) = 1 + \alpha(c)(\lambda - 1).$$

Equation 9

This equation reflects the fact that for a material filled at volume fraction  $c$ , the local strain undergone by the elastomer matrix is  $\alpha$  times greater than the macroscopic strain. Because of strain-induced crystallization, this equation cannot be used to describe the whole tensile curve (not shown here); here it is only applied to strain at break:

$$\Delta_b(c) = 1 + \alpha(c)(\lambda_b - 1).$$

Equation 10

In the following, a two-step approach is considered. First, amplification factors  $\alpha(c)$  are determined for the four unaged materials (four CB contents). Second, these amplification factors are assumed unmodified by ageing and the local strain at break  $\Delta_b$  are contemplated during CR oxidation.

**i) Determination of the local amplification factors on unaged materials**

Assuming that the macromolecular network (without fillers) mainly governs fracture, failure is reached, for all CB contents, at the same value of the local strain  $\Delta_b$ . Thanks to Equation 10, the values of  $\alpha(c)$  for unaged materials are determined such that their respective local strain  $\Delta_b$  are equal. Here we set (arbitrarily)  $\alpha = 1$  for the 10 phr rubber. The corresponding values of  $\alpha$  are presented in Table 3.

Table 3: Identified amplification factors  $\alpha$ . In bold: the calculated values

| CB content (phr) | $\Delta_b$  | Parameter $\alpha$ |
|------------------|-------------|--------------------|
| 10               | <b>7.27</b> | 1                  |
| 15               | 7.27        | <b>1.05</b>        |
| 30               | 7.27        | <b>1.51</b>        |
| 45               | 7.27        | <b>2.66</b>        |

Comparing these parameters with existing literature is challenging because, as stated by Nakajima and Scobbo, each elastomer exhibits “a unique pattern of stretch amplification” [44]. In most of the studies, the amplification factors are calculated from the Guth & Gold model [45], which is proved no longer valid beyond a certain CB content and cannot be used for large strain.

From there, the question is whether our calculated coefficients can predict the fall in local strain at break during ageing.

**ii) Change in local strain at break as a function of ageing**

The local strain at break  $\Delta_b$  are now calculated with the previous coefficients  $\alpha$  and the  $\lambda_b$  values of aged materials (Figure 3b). As  $\Delta_b$  relates to the strain of the unfilled matrix, Lake's approach can be used [20], and  $\Delta_b$  should linearly correlate with the crosslinking density  $v_{\text{matrix}}^{-1/2}$  of the matrix (Figure 10). Figure 12 highlights a strong correlation between these quantities up to 30 phr. This demonstrates that ageing modifies the elastic properties of the elastomer matrix independently of the CB content for large strain (at least up to 30 phr). For higher CB content, deviation is observed suggesting that in the case of 45 phr, the interaction filler/matrix is modified by ageing. To conclude, our method predicts the decline in strain at break of aged materials with any CB content ( $\leq 30$  phr), using tensile tests at break and an amplification factor  $\alpha$ .

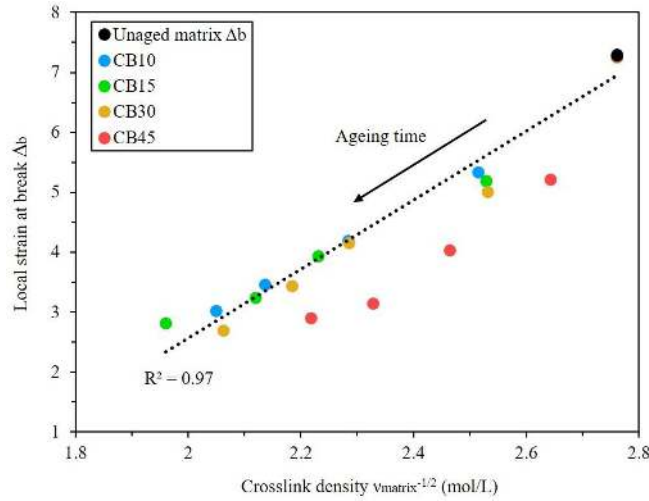


Figure 12: Local strain at break  $\Delta_b$  as a function of crosslink density  $\nu_{\text{matrix}}^{-1/2}$  for all materials, at all ageing conditions

#### 4.2.3. Fatigue life

When we now focus on the impact of ageing on elastomer fatigue, we should first note that The literature is scarce on that topic. In addition, there are no well-established theoretical relationships that directly relate fatigue life to rubber network properties. Nevertheless, it is possible to establish an empirical correlation between the number of cycles to failure  $N$  with the crosslink density during ageing, as demonstrated by previous studies on both unfilled [24] and 15 phr CB-filled CR [19]. Figure 13 shows the fatigue life at  $\lambda = 2$  and  $R = 0$  as a function of the crosslink density of the rubber matrix  $\nu_{\text{matrix}}$ .

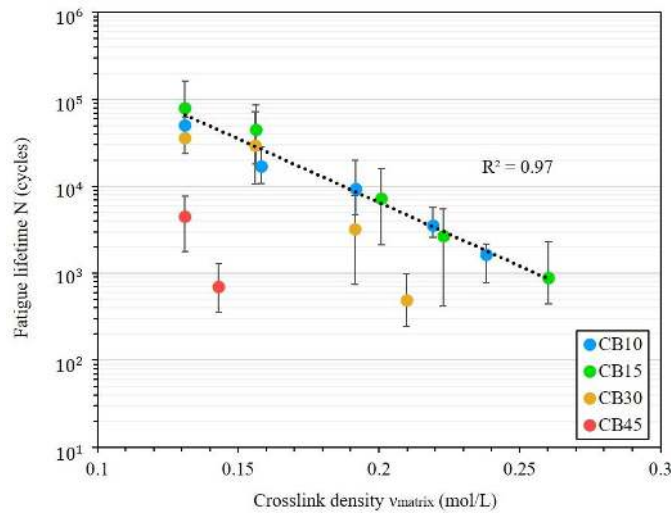


Figure 13: Relationship between fatigue life at  $\lambda=2$  and matrix crosslink density. The dotted line encompasses CB10 and CB15 data only

The correlation is remarkable up to 15 phr fatigue life can be related to the crosslink density of the matrix regardless of the CB content for  $c \leq 0.082$ . Above this CB content, deviations could be due to insufficient particle dispersion in the matrix, potentially leading to a decline in fracture properties [46] [47]. This particle dispersion hypothesis could be tested in future work using various experimental techniques [48]. As explained above, the strain endured by the polymer chains  $\Delta$  varies with  $c$  during fatigue testing, which is not taken into account in Fig. 13. However, we can state that the fatigue life of moderately filled aged CR can be predicted from  $\nu_{\text{matrix}}$  independently of the carbon black content.

## 5. Conclusion

In the present work, thermo-oxidative ageing of carbon black-filled polychloroprene rubbers has been studied. The effect of ageing on mechanical properties has been described by separating the behaviour of materials into the contributions of the unfilled rubber matrix and the carbon black content. It is assumed that the rubber matrix has the same crosslink density for all CB filled unaged formulations and that ageing-induced crosslinking does not depend on the CB content.

Then, our experimental results have been compared with existing strain concentration models to explain ageing of filled rubbers:

- For small strain, the contribution of fillers follows the reinforcement theory of Guth and Gold [2], and the relative increase in stiffness induced by ageing is described.
- For large strain, ageing alters the elastic properties of the rubber matrix independently of the carbon black content. Consequently, the evolution of the macromolecular network is directly linked to the microscopic strain in aged rubber matrix.
- Fatigue life of the aged, moderately-filled materials correlates satisfactorily with the corresponding crosslink density of the rubber matrix.

These findings show that the mechanical properties of CB-filled elastomer can be related to the macromolecular network during oxidative ageing, across a broad range of filler contents. This holds significant potential for predicting the lifetime of elastomers with various formulations. Nevertheless, the results obtained for high carbon black content largely deviate from the predictions. Although they can be accounted by specific fillers parameters [38] for small strain, future work is required for large strain and fatigue loadings.

## CRedit authorship contribution statement

Hugo Madeira: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – Original draft, Writing – Review & Editing.

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

Maeleenn 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.

## Data availability statement

Data will be made available on demand.

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