Archimer
https://archimer.ifremer.fr

***In* Constitutive Models for Rubber X. Proceedings of the European Conference on Constitutive Models for Rubbers X (Munich, Germany, 28-31 August 2017). pp 45-51**
2017
Eds Alexander Lion, Michael Johlitz
ISBN 9781315223278
https://archimer.ifremer.fr/doc/00666/77829/

Comparison between thermo-oxidative aging and pure thermal aging of an industrial elastomer for anti-vibration automotive applications

Broudin M. [1], Marco Y. [2], Le Saux V. [2], Charrier P. [1], Hervouet W. [1], Le Gac Pierre Yves [3]

[1] Vibracoust CAE & Durabil Predict Dept, Carquefou, France.
[2] ENSTA Bretagne Inst Rech Dupuy Lome IRDL, FRE CNRS 3744, Brest, France.
[3] IFREMER French Ocean Res Inst, Lab Comportement Struct Mer, Plouzane, France.

Abstract :

Elastomeric anti-vibration parts found in automotive parts are usually massive, usually, a thickness of 10 mm or more is observed. Aging therefore leads to heterogeneous properties, possibly induced by several mechanisms due to the availability, or not, of oxygen in the part's bulk. To better understand the effects of oxygen in the degradation process, this paper aims at studying the aging of a rubber material (conventional vulcanization system) in aerobic (with oxygen) and anaerobic (without oxygen) conditions for a wide range of temperatures, relevant for under hood applications. A specific protocol to realize aging under anaerobic conditions was defined and validated. The consequences on the mechanical behavior are analyzed throughout monotonic tensile tests and fatigue campaigns results. The effects and kinetics of the two aging conditions are compared. In order to check the hypothesis of a physical aging related to desorption of low molecular weight ingredients, common to both aerobic and anaerobic conditions, a specific investigation is led on a material tested after swelling in toluene.

Please note that this is an author-produced PDF of an article accepted for publication following peer review. The definitive publisher-authenticated version is available on the publisher Web site.

1 INTRODUCTION

1.1 *Industrial and collaboration backgrounds*

Rubber parts for anti-vibration systems are designed to meet several mechanical requirements: efficient damping on given ranges of frequencies, reliable static response over the service time, resistance to creep and fatigue. The automotive applications furthermore require the assessment of these features for thermal conditions inducing aging. This aging is related both to the effect of oxygen but also, for these massive parts, to the effect of temperature only. Several recent features require to go beyond the empirical rules. The first one is an ever reducing development time, which leads to assess compounds more quickly and/or to validate "carry over" strategies (checking that parts previously developped for one manufacturer specification will pass another's ones). A second point is the need to design parts meeting the requirements for any locations on the globe, increasing the severity profiles of users (roads and weather conditions). A last one is connected to the environmental standards (REACH and EURO6) that restrict the use of specific ingredients and lead to higher service temperatures. Integrating efficiently the aging effects in the design loop therefore becomes a crucial need.

This is the task of a research group bringing together ENSTA Bretagne, Chemnitz University of Technology, Freudenberg Technology Innovation and Vibracoustic. In a PhD thesis lead at ENSTA Bretagne, the focus is given on the understanding of the physico-chemical mechanisms and the description of the mechanical consequences of thermo-oxidative aging.

1.2 *Scientific background*

Thermo-oxidative degradation of rubber components is a topic widely investigated in the literature (Bolland & Gee, 1946, Broudin et al., 2015, Herzig et al., 2015, Kamarudding et al., 2011, Naumann & Ihlemann, 2013, Schlomka et al., 2017), because this aging induces severe modifications of the mechanical properties, both for constitutive response (Johlitz & Lion, 2013) and failure properties for monotonic tension (Gillen et al., 2005), crack propagation (South et al., 2003) or fatigue tests (Charrier et al., 2011). Nevertheless, relating the physico-chemical mechanisms to the evolution of the mechanical properties is not

an easy task as many aging mechanisms could be at stake. A first range of mechanisms is of course related to oxidation, leading to strong modifications of the elastomer network (main-chain scissions, crosslink formation and/or crosslink breakage) (Verdu, 2012). Large-sized automotive parts age heterogeneously due to the availability, or not, of oxygen in the part's bulk. This leads to a classical analysis using a DLO approach based on the competition of the kinetics of oxygen diffusion and consumption (Celina et al., 2000). Nevertheless, the hardness profiles observed at the core of thick parts and samples (Le Saux, 2010) also illustrate that aging leads to mechanical changes even without oxygen. Numerous studies investigated the effect of temperature aging in the absence of oxygen on the mechanical properties of rubber materials. A first range of studies investigated the evolution of the tensile properties (Kohman, 1929, Shelton & Winn, 1944) for anaerobic conditions and found a limited increase of stiffness and little reduction of the ultimate tensile properties. Then, Kim et al. (1994) illustrated that the change of fatigue crack growth resistance of carbon-black filled vulcanizates for various heat aging environments leads to higher fatigue crack growth rate evolutions under air than under nitrogen because the oxidative degradation of the rubber causes a high reversion inducing a dominant effect on the mechanical fatigue resistance. This effect is also confirmed by Soma et al. (2010) to a lesser extent. Dealing with fatigue, a recent study showed that a first common drop of fatigue lifetimes can be observed for anaerobic and aerobic conditions, followed by stabilization in the case of anaerobic aging and further degradation for aerobic aging (Broudin et al., 2015). Nevertheless, the origins of these evolutions of the mechanical properties both for stiffness or failure remain unclear. Several explanations could be suggested: plasticizers extraction (Calvert & Billingham, 1979), sulfur network evolution (Kim & Lee, 1994), structural relaxation (Struik, 1978) and/or fillers network evolution (Roychoudhury & De, 1993).

The present paper aims at two objectives. The first one is to provide a more extensive comparison of the mechanical consequences of aging under aerobic and anaerobic conditions, based on the results of monotonic tensile tests and fatigue campaigns. The second one is to better understand the aging mechanisms under anaerobic conditions and to investigate the hypothesis of a physical aging induced by desorption of low molecular species.

2 EXPERIMENTAL SETTINGS

2.1 *Materials*

2.1.1 *Industrial compound*

The material studied here is a carbon black-filled NR/IR blend. Its recipe is given in Table 1.

All samples were made using the same material batch to limit properties scattering due to mixing, for example. This material will be called "C" in the Figures presented here.

2.1.2 *Material without soluble fraction*

To determine the effect of the extraction of the plasticizers during aging, it would be very convenient to consider the same compound but without plasticizers. Nevertheless, a filled material like the one investigated could not be mixed without plasticizers. It was therefore decided to extract the low molecular weight components (including plasticizers) thanks to swelling in toluene. The sample is finally dried in order to get back to a geometry close to the one before swelling. This material will be called "B" in the Figures hereafter.

2.2 *Aging conditions*

2.2.1 *With oxygen*

Aging with oxygen was carried out in ovens with air-flux control. To get reliable tests, several authors noticed the importance to specify the aging conditions, such as the rate of the air and air exchanges (Spetz, 1994). Therefore, to have quite similar aging conditions, all used ovens have been checked in terms of air speed and air renewal rates thanks to an anemometer and according to (ISO 188:2011). During aging, a thermocouple checks the temperature close to the samples and is connected to continuous strip-chart recorders. The Table 2 gives the tested temperatures and durations.

Table 1. Recipe of the industrial compound.

Formulation	
NR	75.00 phr
IR	25.00 phr
Zinc oxide	4.10 phr
Plasticizers	7.00 phr
Carbon black	29.00 phr

Stearic acid	2.00 phr
Antioxidant	3.00 phr
Antiozonant	3.00 phr
Accelerators	1.00 phr
Sulfur	3.38 phr

Table 2. Aging conditions with oxygen.

	Aging temperature [°C]						
	40	50	60	80	100	110	120
Aging duration [days]							0.25
						0.5	0.5
					1	1	1
				3	3	3	3
				7	7		
			14	14	14		
	21	21	21	21	21		
	42	42	42	42	42		
		90	90				
		180	180				
	360	360	360				
		720					

2.2.2 *Without oxygen*

An experimental protocol was developed to achieve aging without oxygen. To package the samples, a multilayer film is used (SIDEC CA40 NF H 00 310 Class IV). This film is impermeable to oxygen and temperature resistant. Wedges are placed such as no bending/torsion of the samples occurs when the vacuum is performed (Fig. 1, on the left). It is worth noting that the wedges material is chosen to present a thermal expansion coefficient close to the one of rubber, in order to avoid any preload due to differential thermal expansions.

Finally, to remove oxygen inside the package, a vacuum chamber machine is used (Audionvac VMS 133) (Fig. 1, on the right).

The Table 3 gives the tested temperatures and durations.

2.3 *Tensile tests campaign*

The samples used are S2 samples. The S2 samples are cut from plate and then placed in oven to carry out the various aging conditions. The tensile tests were achieved on testing machine equipped with a 1 kN load cell. The tests were displacement controlled (grip speed of 200 mm/min). An optical extensometer was used to measure the local elongation. For each aging condition, at least three samples were tested and the results averaged.

2.4 *Fatigue campaign*

Diabolo samples are obtained by injection molding in order to reproduce industrial manufacturing conditions of mass-produced automotive parts. The compound has been cured for 5 min, with a mold temperature set to 165°C. The fatigue tests were displacement controlled at a frequency of 5 Hz to keep a limited heat build-up. All tests were performed at a controlled temperature of 23°C. The fatigue samples geometry and the fatigue protocol have been detailed in a former publication and will not be recalled here (Ostoja Kuczynski et al., 2003).

Figure 1. AE2 sample with PTFE wedges (left); sealed package of AE2 samples for aging without oxygen (right).

Table 3. Aging conditions without oxygen.

	Aging temperature [°C]						
	40	50	60	80	100	110	120
Aging duration [days]						0.5	0.5
				3	3	3	3
				14	14		
	21		21	21	21		
	42	42	42				
					90		
		180	180				

The first test campaign was targeted to investigate the evolution of the fatigue strength at room temperature. To keep a reasonable number of samples despite the numerous investigated aging conditions, for each of them, 5 AE2 samples are aged and then tested in fatigue for a given enforced displacement. In this campaign, 3 levels of displacement have been studied, 4.6 mm, 8.1 mm and 14.7 mm which correspond respectively to strains of 80%, 150% and 280%. These strains are evaluated by FE simulations from the geometry of the unaged sample.

3 RESULTS AND DISCUSSION

3.1 *Aging campaign with oxygen*

On the next page, Figure 2 to 4 (left column) illustrate the results obtained for thermo-oxidative aging. Figure 2 highlights typical results obtained for tensile tests on samples aged in presence of oxygen (here for 80°C and several durations). These observations are valid whatever the aging temperature. One can observe a drop of the strain at break and a stiffening of the mechanical response, which is quite a classical result and could be related to the changes of the vulcanized network. Nevertheless, it should be noted that the evolutions in stiffness and strain at break observed for short durations is already significant. Figure 3 presents the results of the fatigue campaigns for the same aging conditions. The drop of the fatigue lifetime with the aging durations is clearly visible. It is worth noting that the curves keep the same slope, except for the last aging condition, considered to be extremely severe.

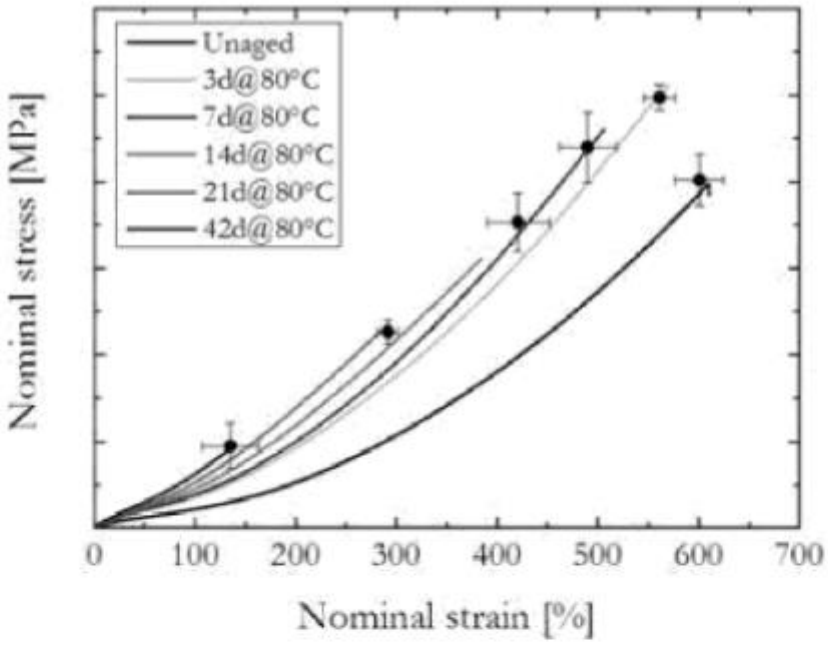

Figure 2. Material C. Aging with oxygen. Tensile test results after various preliminary heat aging (from 3 days to 42 days @ 80°C).

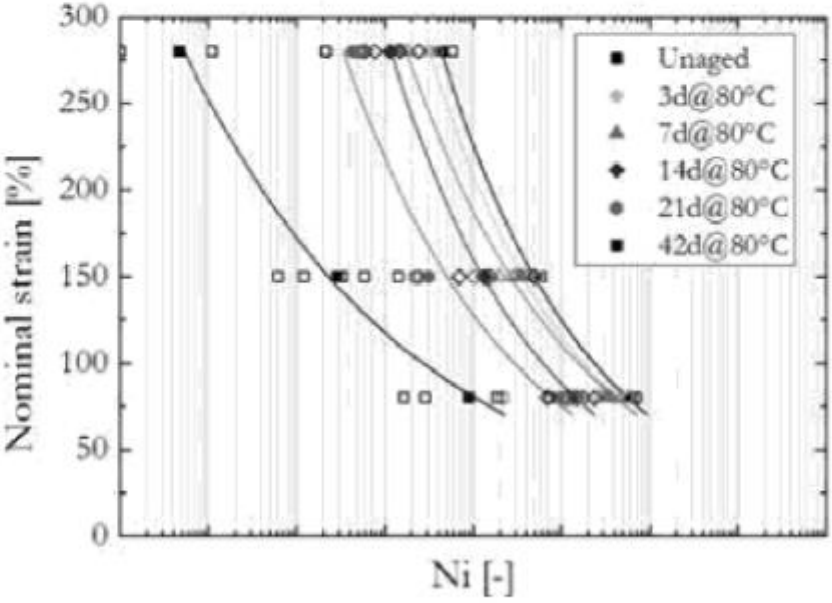

Figure 3. Material C. Aging with oxygen. Wöhler curves after various preliminary heat aging (from 3 days to 42 days @ 80°C).

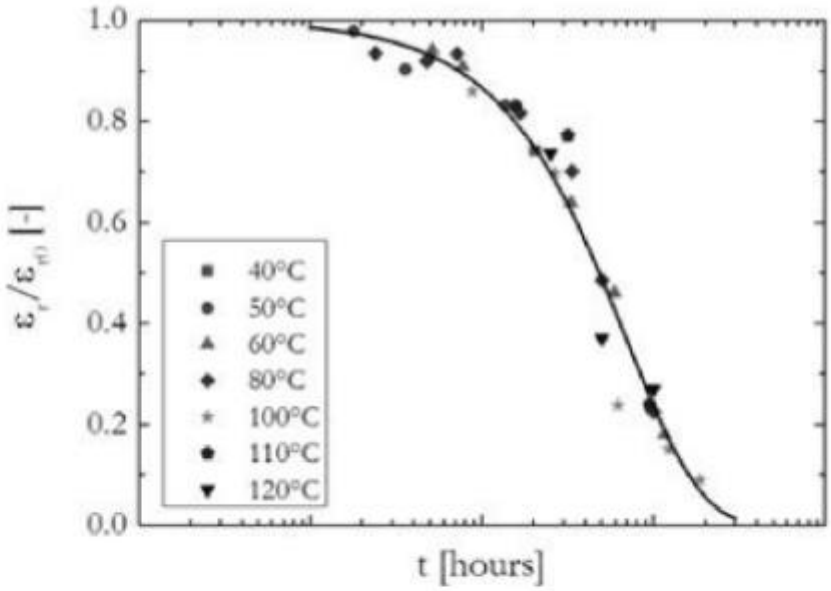

Figure 4. Material C. Aging with oxygen. Master curve obtained on the relative evolution of the strain at break.

A single aging mechanism is clearly not probable for this complex aging. Nevertheless, the identification of a time-temperature superposition seems possible, as illustrated by the master curve obtained on the relative evolution of the strain at break (Fig. 4). The deduced activation energy is of 94 kJ/mol. A comparable result can be obtained from the fatigue tests with an activation energy of 95 kJ/mol (Broudin et al., 2015). Both values are very close to other values found in the bibliography for various aging indicators (Celina et al., 2000, 2005).

3.2 *Aging campaign without oxygen*

On the next page, Figure 5 to 7 (right column) illustrate the results obtained for thermal aging without oxygen. Figure 5 highlights a drop of strain at break and a stiffening of the mechanical response. Both variations seems to occur early and then to stabilize, and are less severe than for oxidative aging. Figure 6 presents the results of the fatigue campaigns for the same aging conditions. Here again, the drop of the fatigue lifetime with the aging durations occurs early and then stabilizes to a level much less severe than for long oxidative conditions.

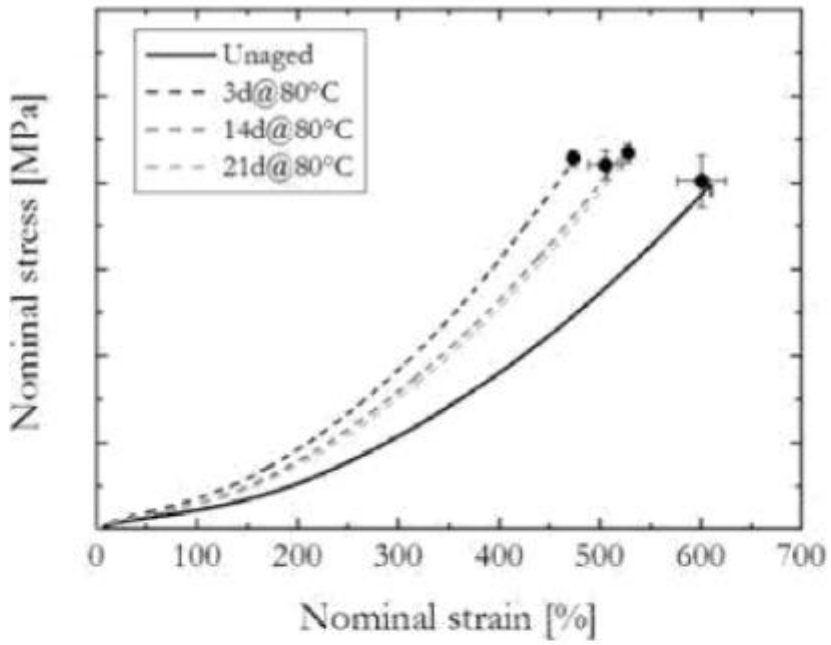

Figure 5. Material C. Aging without oxygen. Tensile test results after various preliminary heat aging (from 3 days to 21 days @ 80°C).

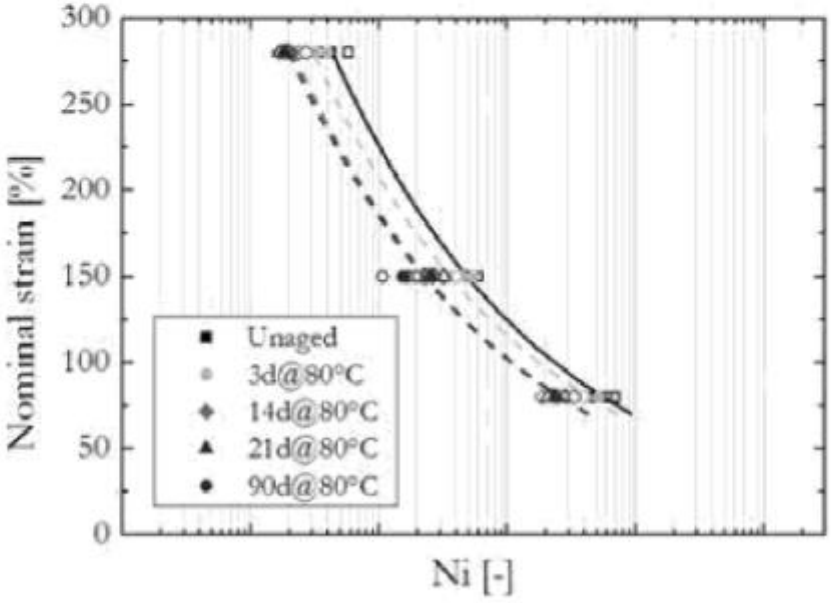

Figure 6. Material C. Aging without oxygen. Wöhler curves after various preliminary heat aging (from 3 days to 90 days @ 80°C).

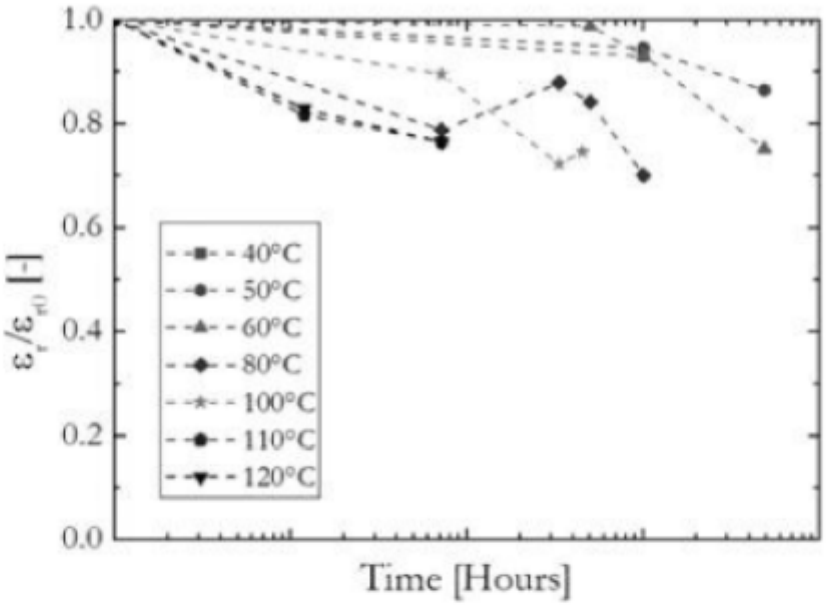

Figure 7. Material C. Aging without oxygen. Relative evolutions of the strain at break.

The identification of a time-temperature superposition seems in this case not possible, as illustrated on Figure 7.

3.3 *Comparison of the results obtained after both aging protocols and also to the results obtained for samples after swelling in toluene*

Figure 10 summarizes the evolution of the relative strain at break for tensile tests performed on samples after aerobic and anaerobic aging durations at 80°C. Figure 11 provides the same synthesis for the variations of the relative fatigue lifetime (for a given enforced displacement). One can observe on these curves that the drops of tensile and fatigue properties seem to present a common kinetic for the early aging durations. Then, the loss of the failure properties reaches a stabilized level for the aging conditions without oxygen, whereas the loss of failure properties continues for the aging conditions with oxygen.

In order to check if this common initial drop of tensile and fatigue properties, for conditions with or without oxygen, could be related to the extraction of plasticizers, tensile and fatigue tests have been performed on the material after swelling in toluene.

It should be underlined here that the results obtained are presented for 80°C only due to the restricted format of the paper, but similar conclusions can be drawn from the results obtained for lower and higher aging temperatures like

60°C and 100°C.

Figure 8 illustrates that, for tensile tests, the material after swelling in toluene presents a mechanical response and a strain at break consistent with the material aged without oxygen at 80°C after 14 days. The curve obtained for the same temperature and duration but under oxidative aging, presents a higher stiffening and a lower ultimate tensile strain.

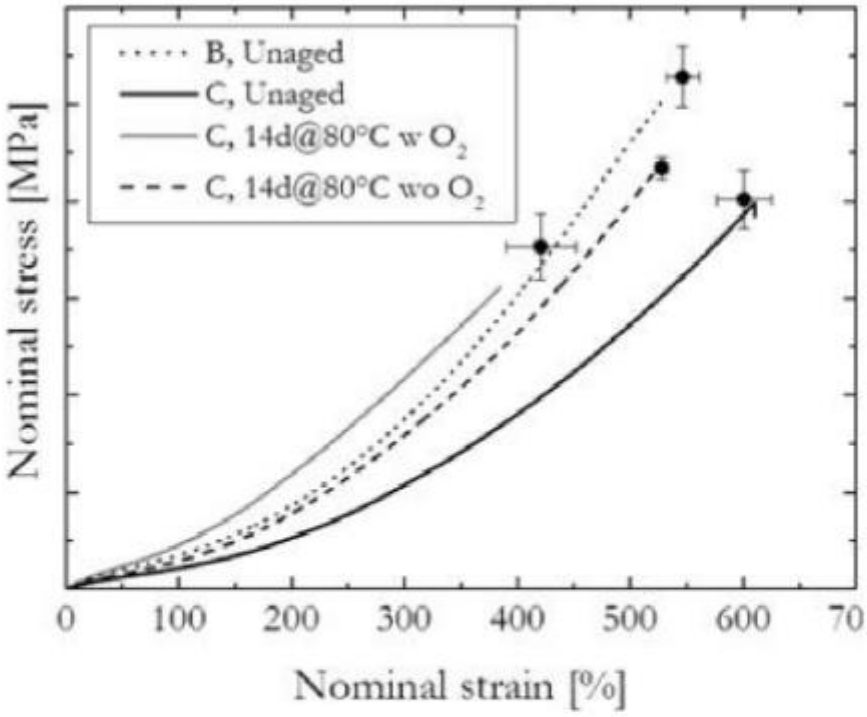

Figure 8. Tensile curves obtained after aging with and without oxygen at 80°C for 14 days and after swelling in toluene (mat. B).

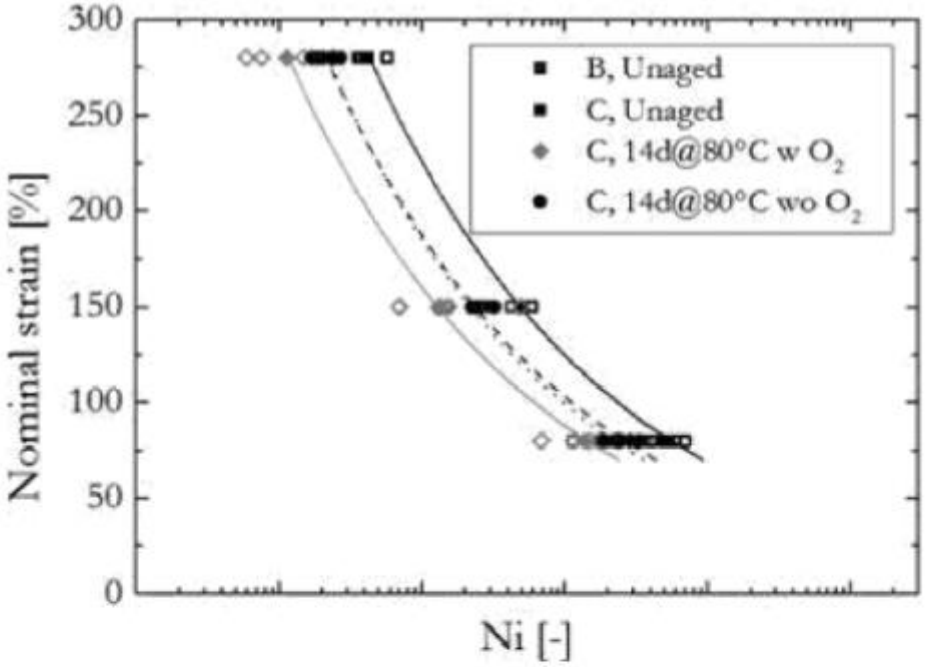

Figure 9. Fatigue curves after aging with and without oxygen at 80°C for 14 days and after swelling in toluene (mat. B).

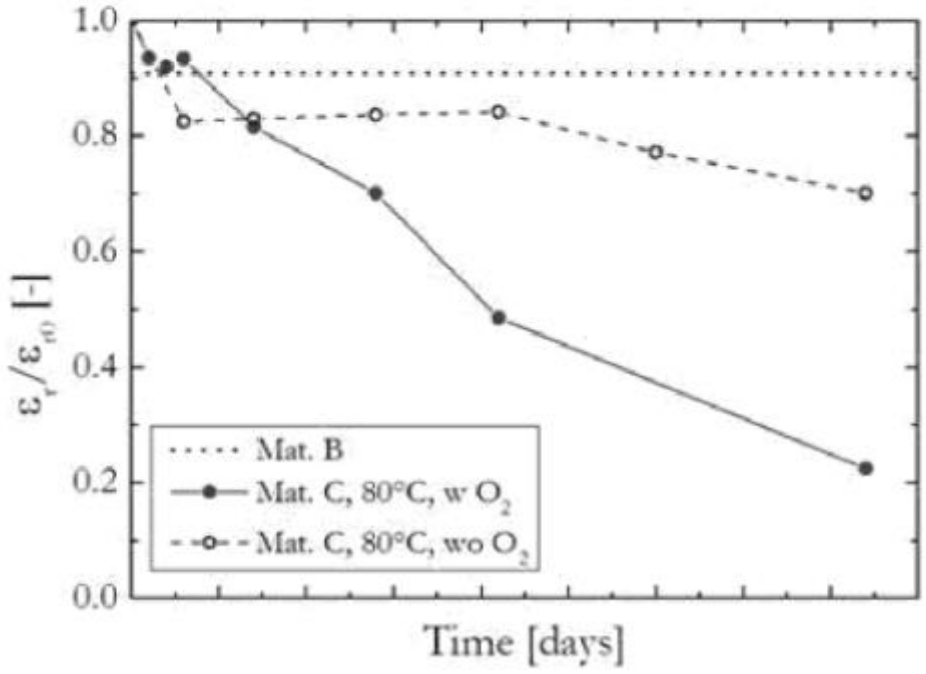

Figure 10. Evolution along time of the relative strain at break obtained after aging with and without oxygen at 80°C and after swelling in toluene (mat. B).

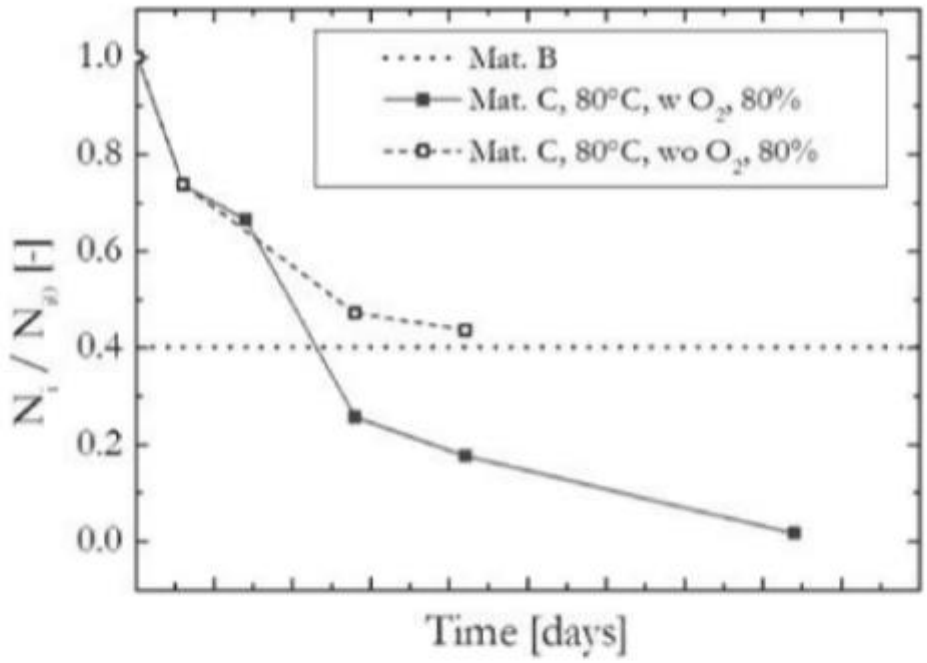

Figure 11. Evolution along time of the relative fatigue lifetime obtained after aging with and without oxygen at 80°C and after swelling in toluene (mat. B).

Figure 9 presents the results of the fatigue campaigns, for the same aging conditions. Here again the drop of the fatigue lifetime for the sample after swelling in toluene seems to correlate well with the one observed for aging without oxygen.

In order to check these first comparisons, the values obtained for the samples tested after swelling in toluene were compared with the evolutions of the samples aged with or without oxygen. These comparisons are illustrated in Figure 10 and 11 as the dotted line is the value obtained for the samples tested after swelling in toluene.

Figure 10 and 11 illustrate that the drop of strain at break and fatigue lifetime for anaerobic conditions stabilize for values correlated to the ones obtained for the material after swelling in toluene. It therefore seems that the initial drops of strain at break and fatigue properties observed both under aerobic and anaerobic conditions seem well correlated to the loss of low molecular weight components. The nature of these components is still to be determined even if it seems very probable that they are plasticizers. TGA and GC-MS measurements are currently done in order to clarify this point.

4 CONCLUSION AND PERSPECTIVES

In this paper, we focus on the aging of a rubber material (conventional vulcanization system) in aerobic (with oxygen) and anaerobic (without oxygen) conditions, over a wide range of temperatures relevant for under hood applications. Tensile and fatigue tests are analyzed. For both aging cases, progressive drops of the strain at break and the fatigue properties are observed as well as a progressive increase of the stiffness. Under anaerobic and aerobic conditions, these evolutions seem to exhibit the same kinetics for the short durations. Nevertheless, the evolution of the mechanical indicators reaches a plateau for anaerobic aging, whereas the evolutions go on for aerobic aging.

In order to investigate if these evolutions can be related to a physical aging induced by the extraction of low molecular weight components (plasticizers, for example), tensile and fatigue tests have been performed on samples after swelling in toluene. It appears that the values obtained on these samples are well correlated to the plateau observed for anaerobic aging. This hypothesis seems therefore reasonable and this mechanism could be common to aging conditions with or without oxygen.

Further investigations are running to identify the nature of the components extracted in toluene and to understand better the other possible aging mechanisms at stake, both for anaerobic and aerobic aging.

ACKNOWLEDGEMENTS

The authors would like to thank Vibracoustic for its financial support and all the partners, ENSTA Bretagne—IRDL, Freudenberg Technology Innovation, and Chemnitz University of Technology. A special thanks to Pierre-Yves Le Gac from IFREMER for fruitful scientific discussions and technical support.

REFERENCES

Bolland, J.L. & Gee, G. 1946. Kinetic studies in the chemistry of rubber and related materials. II. The kinetics of oxidation of unconjugated olefins. Trans. Faraday Soc. 42, 236–243.

Broudin, M., Le Saux, V., Marco, Y., Charrier, P., Hervouet, W. 2015. Investigation of thermal aging effects on the fatigue design of automotive antivibration parts. In ECCMR IX, 53–59. CRC Press.

Calvert, P.D. & Billingham, N.C. 1979. Loss of additives from polymers: A theoretical model. J. Appl. Polym. Sci. 24, 357–370.

Celina, M., Gillen, K.T., Assink, R.A. 2005. Accelerated aging and lifetime prediction: Review of non-Arrhenius behaviour due to two competing processes. Polym. Degrad. Stab. 90, 395–404.

Celina, M., Wise, J., Ottesen, D., Gillen, K.., Clough, R. 2000. Correlation of chemical and mechanical property changes during oxidative degradation of neoprene. Polym. Degrad. Stab. 68, 171–184.

Charrier, P., Marco, Y., Le Saux, V., Ranaweera, R.K.P. 2011. On the influence of heat ageing on filled NR for AVS automotive applications. In ECCMR VII, 381–387. CRC Press.

Gillen, K.T., Bernstein, R., Derzon, D.K. 2005. Evidence of non-Arrhenius behaviour from laboratory aging and 24-year field aging of polychloroprene rubber materials. Polym. Degrad. Stab. 87, 57–67.

Herzig, A., Johlitz, M., Lion, A., 2015. Experimental investigation on the consumption of oxygen and its diffusion into elastomers during the process of ageing. In ECCMR IX, 23–28. CRC Press.

ISO. Caoutchouc vulcanisé ou thermoplastique—Essais de résistance au vieillissement accéléré et à la chaleur. ISO 188:2011, 20.

Johlitz, M. & Lion, A. 2013. Chemo-thermomechanical ageing of elastomers based on multiphase continuum mechanics. Contin. Mech. Thermodyn. 25, 605–624.

Kamarudding, S., Le Gac, P.Y., Marco, Y., Muhr, A. 2011. Formation of crust on Natural Rubber after long periods of ageing. In ECCMR VII, 197–201. CRC Press.

Kim, S.G. & Lee, S.-H. 1994. Effect of crosslink structures on the fatigue crack growth behavior of NR vulcanizates with various aging conditions. Rubber Chem. Technol. 67, 649–661.

Kohman, G.T., 1929. The Absorption of oxygen by rubber. J. Phys. Chem. 33, 226–243.

Le Saux, V., 2010. Fatigue et vieillissement des élastomères en environnements marin et thermique: de la caractérisation accélérée au calcul de structure. Université de Bretagne Occidentale—Brest.

Naumann, C., Ihlemann, J. 2013. Chemomechanically coupled finite element simulations of oxidative aging in elastomeric components. In ECCMR VIII, 43–49. CRC Press.

Ostoja Kuczynski, E., Charrier, P., Verron, E., Marckmann, G., Gornet, L., Chagnon, L. 2003. Crack initiation in filled natural rubber: experimental database and macroscopic observations. In ECCMR III, 41–47. CRC Press.

Roychoudhury, A., De, P.P. 1993. Reinforcement of epoxidized natural rubber by carbon black: Effect of surface oxidation of carbon black particles. J. Appl. Polym. Sci. 50, 181–186.

Schlomka, C., Ihlemann, J., Naumann, C., 2017. Simulation of oxidative aging processes in elastomer components using a dynamic network model. In ECCMR X (in press).

Shelton, J.R., Winn, H. 1944. Aging of GR-S vulcanizates in air, oxygen, and nitrogen. Ind. Eng. Chem. 36, 728–730.

Soma, P., Tada, N., Uchida, M., Nakahara, K., Taga, Y. 2010. A Fracture mechanics approach for evaluating the effects of heat aging on fatigue crack growth of vulcanized natural rubber. J. Solid Mech. Mater. Eng. 4, 727–737.

South, J.T., Case, S.W., Reifsnider, K.L. 2003. Effects of thermal aging on the mechanical properties of natural rubber. Rubber Chem. Technol. 76, 785–802.

Spetz, G. 1994. Improving precision of rubber test methods: Part 2 — ageing. Polym. Test. 13, 239–270.

Struik, L.C.E. 1978. Physical aging in amorphous polymers and other materials. Elsevier, New York.

Verdu, J., 2012. Oxidative ageing of polymers. Wiley-ISTE, London.