High Temperature Effects on Black Carbon Filled NR/SBR Elastomer Behavior

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***Abstract*— In the present work, the effect of high temperatures on an Natural Rubber/Styrene Butadiene Rubber (NR/SBR) mixture behavior was studied. Thus, uni-axial tensile tests and Differential Scanning Calorimetry (DSC) analyzes on virgin and aged specimens at different temperatures were realized. Later, Scanning Electron Microscopy (SEM) micrographs were made to examine fracture facies and thermal aging influence on the elastomer surface morphology. The results obtained showed that the mechanical properties of the material deteriorate when the thermal aging is more severe. Indeed, high temperature led to rapid degradation of the studied NR/SBR mixture. This loss of elasticity is due to the increase in thermal stability, resulting from a decrease in chains' mobility. Moreover, DSC analyzes revealed that the glass transition temperature tended to increase with aging time and temperature. Changes in mechanical properties seem to be in good agreement with the SEM obtained micrographs, where structural alteration is recorded under high temperatures. In conclusion, mechanical and structural behavior of the studied elastomer was significantly altered by high temperature.**

Keywords—Thermal aging, Filled elastomer, Mechanical properties, Glass transition temperatures.

I. INTRODUCTION

Recently, elastomers are increasingly used in many industrial applications such as automotive (anti-vibration parts, tires, silent blocks, etc.). Indeed, the particular nature of such polymers in chained forms as well as their assemblage modes' variety originate the high diversity of their applications. Using elastomers in industry is widespread due to their interesting mechanical properties. They convey many functional benefits such as tightness, high deformability and damping [1-2]. Moreover, their low cost and implementation ease are two factors favoring their industrial development [3]. However, elastomers are exposed to different damaging threats that can occur simultaneously. According to the severity of the exposure conditions, a decrease in the rubber durability is observed [4-6]. This durability loss under physical aging leads to mechanical degradation, while chemical aging causes irreversible chemical degradation. Therefore, the use of elastomers under high temperature greatly affects their tenacity. Indeed, thermal lifting is one of the main encountered failure modes for such material [4-8]. Thus, a dimensioning of elastomeric parts sought under high temperature is necessary. However, elastomeric structures lifetime is still misunderstood. To overcome this deficiency, often important safety factors are used in elastomers dimensioning to ensure the functioning safety. This is why elastomers resistance to high temperature and under monotonous and/or cyclic loading becomes a major industrial problem. An improvement of the dimensioning current tools seems to be necessary for a better understanding of the different deterioration phenomena that causes rubber parts rupture [2]. Similarly, the understanding of elastomers performance and the durability under thermal aging represent an important scientific and industrial issue.

Herein, we examined the effect of thermal aging on the durability of an industrial-type mixture, especially used for the manufacture of automobile suspension parts. The mixture is composed of two basic elastomers [natural (NR) and synthetic (SBR)]. The whole is loaded with 10% (w/w) of black of carbon. For this, samples were heat aged at 50, 70 and 100°C for 3, 6, and 9 days, respectively. Finally, the influence of temperature and time of exposure to heat were then examined through uniaxial tensile tests, Differential Scanning Calorimetry (DSC) analyzes, and Scanning Electron Microscopy (SEM).

II. EXPERIMENTAL PROCEDURES

A. Material

The material used in this study is produced by mixing two components: the Natural Rubber (NR) and the Styrene Butadiene Rubber (SBR), filled by 10 weight percent of carbon black, delivered by the TRECYPLAST company, Algeria. This material was obtained by Sulphur vulcanizing process. The resulting plaques were nominally 2 mm of thick. The formulations of the mix are given in Table I.

TABLE I. CHEMICAL FORMULATION OF STUDIED MATERIAL.

Components	(%)
NR	36.30
SBR	13.31
Black Carbon (N550)	10
$CaCo_3$	22.2
Zinc oxide	2
Stearic acid	0.7
Sulphur	2
CBS	1.7
Stabilizer agent	6
Aromatic oil	5
Others	0.79

Even though for characterizing the materials behavior, uniaxial tensile test have been carried out. These tests were performed in order to get the stress–strain relationship and the ultimate properties (in terms of strain and stress at break). H2 dumbbell specimens were taking according to the ISO 37-2 test standard [7]. Fig.1 shows the specimens geometry. Note that the thickness of these specimen kinds is 2 mm and were cut from plates using a die set.

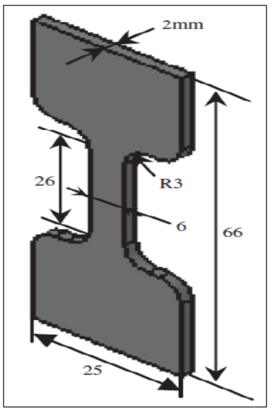

Fig. 1. ISO 37-2 tensile specimen geometry.

B. Thermal aging

Thermal aging experiments were performed in a convection oven, under 50°C, 70°C and 100°C during 3, 6, and 9 days, respectively. The ISO 188 standard describes all thermal conditions aging of vulcanized rubbers [8].

A. Uni-axial tensile tests

The uniaxial tensile tests were conducted using a LLOYD universal machine, type EZ.20 AMETEK, equipped with a load cell of 5 kN. It is very well adapted to highly deformable materials such as elastomers since their cross can reach a displacement of one meter. The tests were performed at a crosshead displacement rate of 10 mm/min. Displacements were measured using two extensometers that delimited the ultimate zone of specimen (26 mm). The tensile specimens are keeping in a system of bit with automatic tightening until fracture without slip.

B. SEM Micrographs

Microscopic observations have been investigated using Scanning Electronic Microscopy (SEM), in order to study the fracture facies of fractured specimens before and after their thermal aging. For that, a thin layer of gold has been deposited in order to increase their electrical conductivities.

C. DSC Analyzes

Differential Scanning Calorimetry analyzes was used to follow the progression of the thermochemical behavior of the material as well as the glass transition temperature throughout the exposure to heat.

III. Results and Discussions

A. Uni-axial tensile tests

In order to analyze the influence of thermal aging on the overall mechanical behavior and to see the variations of the intrinsic properties (stress and elongation at break), we plot the curves (Stress-Strain) in true values for the different conditions of aging. Figures 2.a, 2.b and 2.c illustrate the evolution of the true stress as a function of the true strain of the vulcanized (Unaged) study material and the aged at 50°C, 70°C and 100°C for 3, 6 and 9 days, respectively. The resulting curves exhibit a similar appearance while the behavior of the virgin material is nonlinear, hyper-elastic and flexible transforming progressively under the influence of aging into a linear, hyper elastic and relatively rigid behavior. Two domains can then be distinguished: (i) a softening zone with intermediate deformations where the evolution is linear thus making it possible to calculate the elastic modulus, and (ii) a curing zone. Also, we observe that the mechanical properties of the material decrease as the time and temperature increase. From that, we can deduce that the effect of thermal aging is the same for the different temperature ranges.

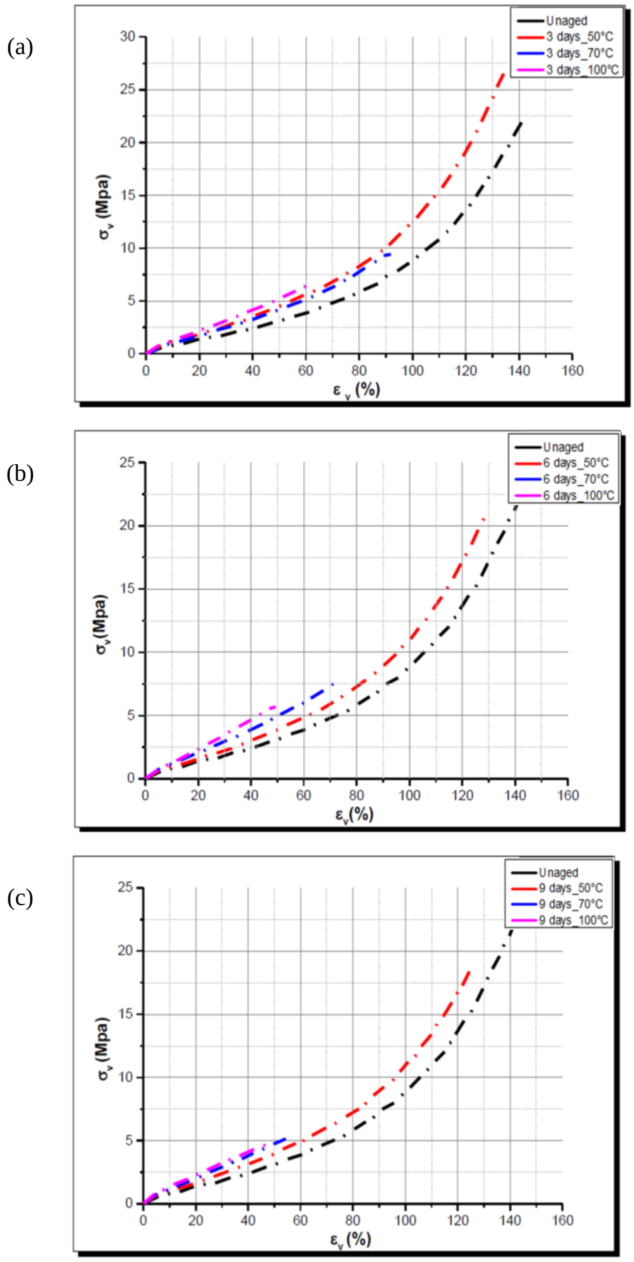

Fig. 2. Evolution of true stress vs true strain with the aging temperature at (a) 3, (b) 6 and (c) 9 days.

The relative comparison of aged properties at breakage show a little impact of aging duration compared to the temperature conditions. Modest changes were observed at 3 days for different aging temperatures. On the other hand, thermal aging at 100°C had an apparent impact on the deterioration of mechanical properties. Accordingly, the high temperature aging seems to have a strong effect on the mechanical properties: higher is the aging temperature more important is the mechanical degradation. These findings are in good agreement with the results recently obtained by Guermazi et al. [9] and Boubakri et al. [4] when studying the effect of aging time and temperature on thermoplastic polyurethane and polyethylene coating. In fact, thermal aging allows to a molecular rearrangement due to heat exposition lead to modification of stress–strain properties of mixtures which seem to be very sensitive to temperature: elongation at break decreased while tensile strength and initial modulus increased, mainly due to crosslinking or chain scission [4-5, 9-12]. The distinction between the two is made by measuring the elastic modulus.

B. SEM Micrographs

A fracture surface analysis of dumbbell specimen (H2) was carried out by Scanning Electron Microscope. Signs of degradation of the material following thermal aging leading to the rupture are checked. Figure 3.a and 3.b show micrographs of the virgin study elastomer.

(a)

(b)

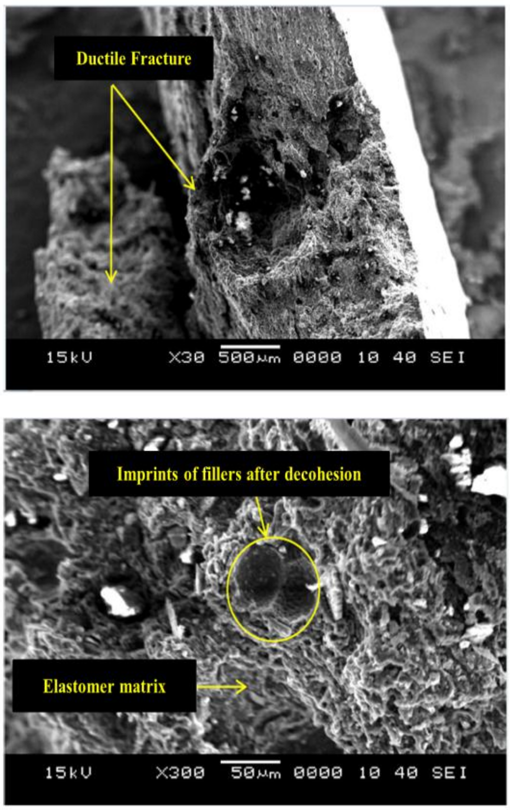

Fig. 3. Fracture facies of unaged material (a) ductile fracture and (b) imprints of the fillers after decohesion.

Figures 4.a, 4.b and 4.c are SEM micrographs which show the microstructures of aged material at 50°C, 70°C and 100°C, respectively. By analyzing fracture facies of broken specimens, it was found that the unaged and aged material has a heterogeneous structure, with ductile and roughened surface which tends to become more and smoother on the side of the outer surface. This transformation is indicating an increasingly fragile break after aging. It is also noted that the surfaces are porous with the presence of different types of fillers.

The obtained results are in concordance with those obtained by Brown et al. [13]. In their work about the main causes of monotonous loading failure of filled synthetic rubber, they found that the main failure mechanisms are: decohesion of the particles, strong presence of micro-voids and micro fissures which essentially propagate from fillers.

(a)

(b)

(c)

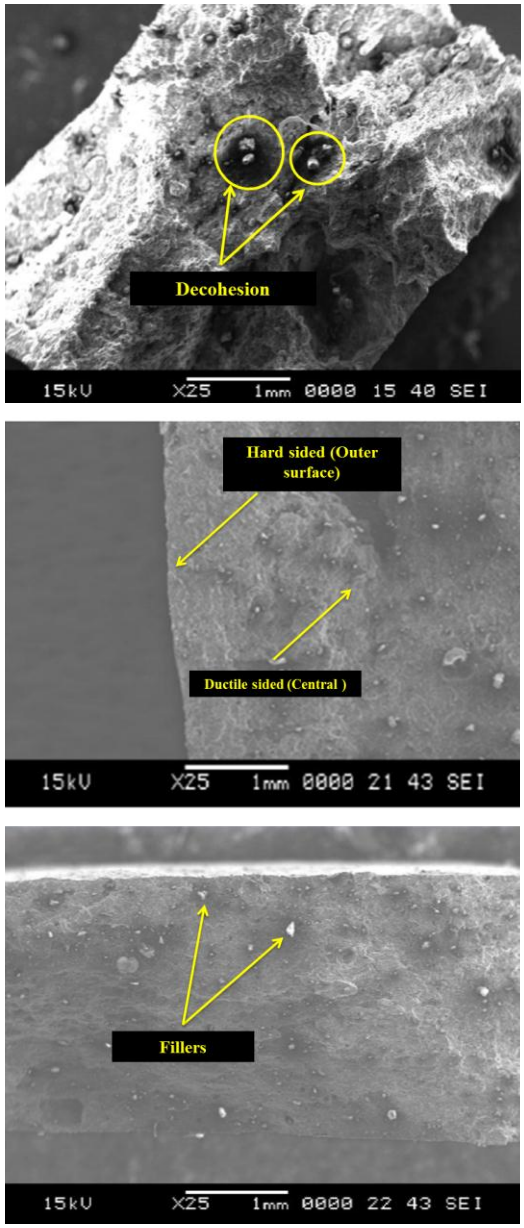

Fig. 4. Surface morphology of aged material at (a) 3 days_50°C (b) 6 days_70°C (c) and 9 days_100°C.

DSC Analyzes

Figures 5.a, 5.b and 5.c show, respectively, the diagrams obtained by DSC at different thermal aging conditions.

From the DSC curves, it can be clearly seen the presence of two glass transition temperatures (Tg_1, Tg_2) between -80°C and -40°C which correspond to the glass transition temperatures of NR and SBR elastomer, respectively. According to Merlin [1], the theoretical values of the glass transition temperatures of NR and SBR are -65°C and -48°C, respectively. In our case, the obtained values are in the same order (-61.42°C and -41.42°C). Note also the presence of a third (Tg) at about (-8.31°C) thus indicating the presence of a phase corresponding to a non-manufacturer given components. At 50°C, a transition is observed, and probably corresponds to a structural relaxation or at the beginning of the degradation caused by the exceeding of the maximum use temperature of the two main elastomers estimated at 50°C.

(a) (b) (c)

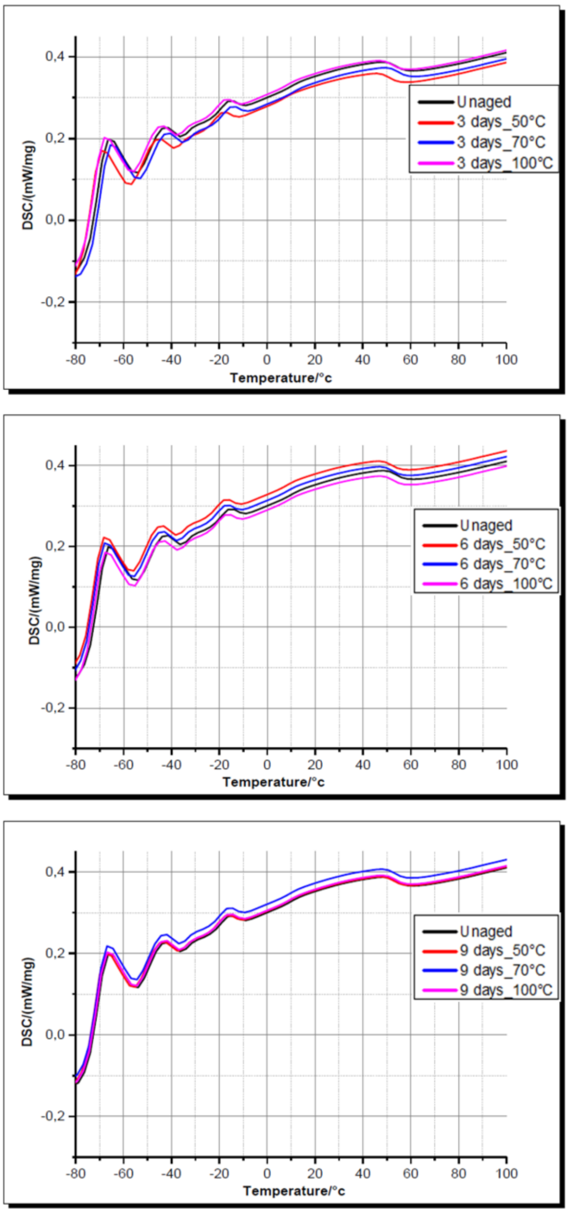

Fig. 5. DSC Thermogram for (a) 3, (b) 6 and (c) 9 days.

To better visualize the results obtained, the progression of the glass transition temperature (Tg) of NR and SBR has been plotted (Fig. 6). The glass transition temperature varies in the same way. At 50°C, A progressive decrease is observed due to the increase of the free volume and chain scission in the material. On the other hand, an increase is recorded at 70°C and 100°C. However, all these values remain below the reference temperatures found for unaged material, except aged samples at 70°C for 3 days. According to the DSC analysis for all thermal conditions, we can conclude that the chain-scission reactions dominate the degradation process, and causing the fall of the material properties.

IV. Conclusion

The effects of aging, especially high temperature, on the mechanical, thermochemical and microstructural properties of the study material were examined. For that, different aging times and temperatures have been selected. The results of the tensile tests have shown that the aging conditions influence considerably the mechanical behavior of the study rubber.

(a) (b)

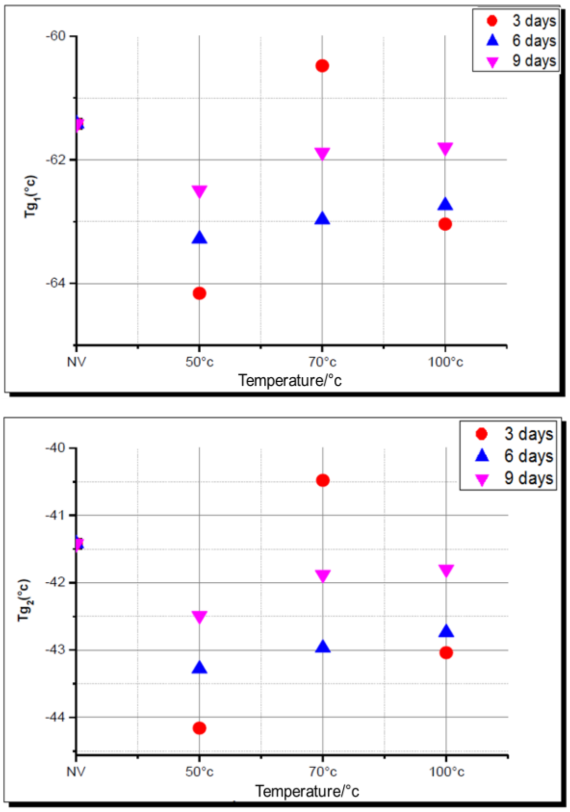

Fig. 6. Tg Evolution at differentes thermal conditions.

Indeed, a decrease in stress and elongation at break, depending on the severity of aging, is recorded. In the same way, the micrographs obtained by SEM, allowed us to note the structural modification on aged material morphology. In fact, the material becomes more and more fragile when exposed to thermal aging. Similarly, DSC analyzes allowed us to understand the different phenomena that may occur during thermal degradation of an elastomeric material.

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