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Pierre Garnier, Jean-Benoit Le Cam, Michel Grediac. Payne Effect In Filled Nitrile Rubber Submitted To Cyclic Loadings. ASME 2012 11th Biennial Conference on Engineering Systems Design and Analysis, Jul 2012, Nantes, France. 10.1115/ESDA2012-82517 . hal-01148139

**HAL Id: hal-01148139**

**<https://hal.science/hal-01148139>**

Submitted on 7 May 2020

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# PAYNE EFFECT IN FILLED NITRILE RUBBER SUBMITTED TO CYCLIC LOADINGS

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## ABSTRACT

This study deals with the viscoelastic properties of filled nitrile rubber submitted to cyclic loading conditions. Classic strain amplitude sweeps were first carried out on both a filled and an unfilled nitrile rubber. Tests were performed at two temperatures ambient and 80 °C. Some specimens were then subjected to a high number of cycles to study the variations in the viscoelastic properties and the sensitivity of the Payne effect to cyclic loading tests at several given strain amplitudes.

## INTRODUCTION

Rubber components are widely used in various fields of engineering, such as the automotive industry and aeronautics, due to their high elasticity and high damping properties. The optimal design of such components must take into account the mechanical properties of rubber (see for instance [1–5]), including viscoelasticity. Classically, the viscoelastic properties of filled rubber are studied using Dynamic Mechanical Analysis (DMA) or Dynamic Mechanical and Thermal Analysis (DMTA). This type of analysis provides the storage modulus  $E'$ , the viscous modu-

lus  $E''$ , and the loss factor  $\tan(\delta)$  for a given double strain amplitude (DSA, defined as the peak-to-peak amplitude). In filled rubber materials, a decrease in the storage modulus is generally observed if the amplitude of the cyclic strain increases. This phenomenon, called the Payne effect [6] or the Fletcher-Gent effect [7], is not observed in unfilled rubber. Several studies have investigated the effect of degradation processes, such as irradiation or temperature for instance [8, 9], on the mechanical properties of rubbers. Nevertheless, the effect of cyclic loading on viscoelastic properties has never been studied in the Payne effect strain domain. This lack of information is quite surprising, since rubber parts are subjected to such mechanical cyclic loading in many industrial applications. This paper aims to investigate variations in the viscoelastic properties of filled nitrile rubber under cyclic loading, typically up to  $10^6$  cycles. These mechanical cycles were applied under compression. This distinguishes all the more singularly the present study, given that the viscoelastic properties of rubber are classically defined under tensile loading. First, material behaviour was characterized using classic DMTA. Second, several DSAs were applied in order to observe and discuss the variations in material behaviour with respect to the number of cycles. Once the mechanical behaviour

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has been characterized at various DSAs, it becomes possible to discuss the evolution of the Payne effect at a given number of cycles. The effect of temperature was also investigated by performing the experiments at ambient temperature and 80 °C. The material, the specimen geometry and the loading conditions are presented first. Then the obtained results are discussed. Finally, some perspectives are given for future work.

## EXPERIMENTAL SETUP

The dynamic properties of both filled and unfilled rubber were measured by means of a Metravib VA2000 viscoanalyzer, using specimens featuring a height of 10 mm and a square cross-section of  $5 \times 5 \text{ mm}^2$ . Classic DMTA was first carried out with filled and unfilled nitrile rubbers. It consisted in applying first an increasing double strain amplitude (denoted DSA in the following) sweep from 0.1 to 15 %, and then a decreasing DSA sweep from 15 to 0.1 %. The DSA sampling satisfied a logarithmic distribution, as in Refs. [10, 11]. This choice is justified by the fact the Payne effect is the most significant for the lowest DSA. The cycle defined by an increasing followed by a decreasing DSA sweep was repeated ten times. The tests were performed at a constant frequency of 10 Hz. The influence of the temperature on the mechanical response was assessed by performing tests at ambient temperature (20 °C in the present case) and 80 °C. Two types of loading conditions were applied: tensile and compressive. In both cases, the mechanical properties were evaluated in terms of  $E'$ ,  $E''$  and  $\tan(\delta)$ , and their evolutions along the tests were recorded.

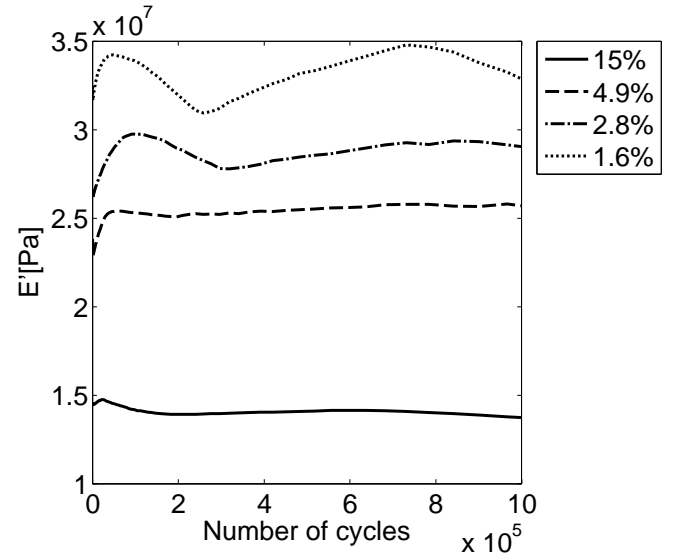
## RESULTS

### Classic DMTA

In light of the DMA experiments previously performed, filled nitrile exhibits a mechanical response in good agreement with those reported in the literature vis-à-vis the Payne effect [10–12]: the increase in temperature causes the Payne effect to vanish. Indeed, the thermal activation allows the macromolecules to slip easily between each other and in the vicinity and within the filler agglomerates. It also impairs the initial stiffness. Finally, the type of loading conditions changes the relative position between successive sweeps and the values of  $E'$ , but the Payne effect itself is not really affected.

### Cyclic loading tests at ambient temperature

The effect of the mechanical cycles on the visco-elastic properties is now considered. The phenomena that are observed will be interpreted in light of the chemical and physical evolutions that likely appeared in the tested specimens. Since the previous paragraph shows that fillers influence the viscoelastic properties of the material, only the filled nitrile is examined here.



**FIGURE 1.**  $E'$  VERSUS THE NUMBER OF CYCLES AT AMBIENT TEMPERATURE, FOR THE FOUR DSA CONSIDERED

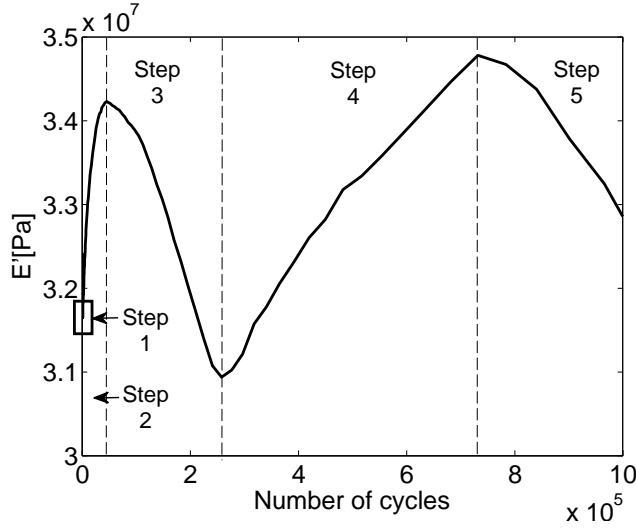
Figure 1 shows the evolution of  $E'$  at ambient temperature during the tests. Each DSA previously applied was applied again, but for the sake of simplicity, only four typical curves are plotted in the diagram.

The first remark is that whatever the number of cycles, the higher the strain amplitude, the lower the storage modulus. This is a first analogy with the Payne effect discussed previously. The second observation is that apart from the highest DSA level (15 %), the initial level of  $E'$  is lower than the final one. This is somewhat unusual since cyclic mechanical loading generally induces a decrease in  $E'$ . Another interesting feature is that all curves obtained can be seen as a succession of five elementary steps, which are reported in Fig. 2.

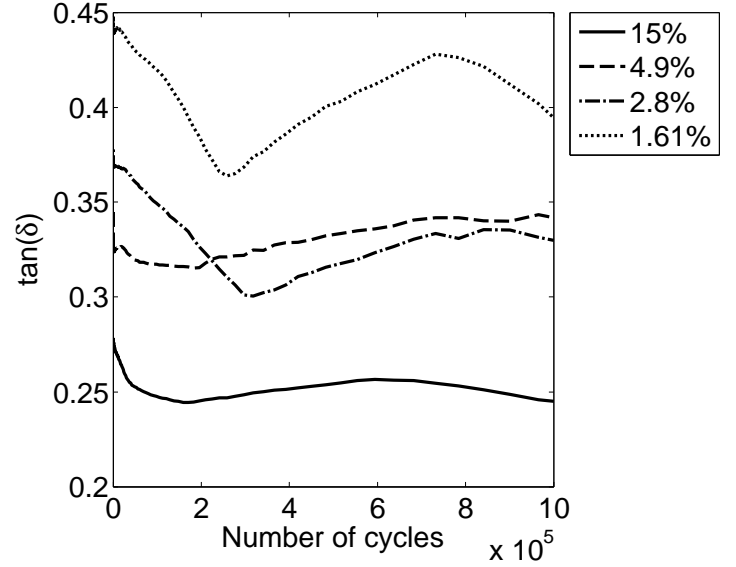
The first step, called step 1 in the following, only occurs during the very early stages of the tests. It corresponds to a decrease in  $E'$ , which can be observed in Fig. 3. This first step can be considered as a material softening.

The combined variations of both  $E'$  (Fig. 1) and  $\tan(\delta)$  (Fig. 4) during the four following steps are more clearly visible by normalizing the curves. This normalization is performed by dividing  $E'$  and  $\tan(\delta)$  by their respective maximum values. The corresponding diagram, illustrating the normalization for the particular case of 2.8 % DSA, is given in Fig. 5.

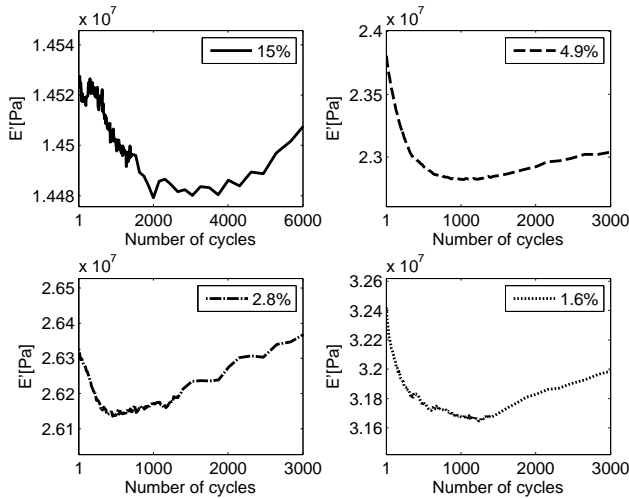
After a decrease in  $E'$  during step 1, step 2 corresponds to a strong increase up to a maximum value reached at  $4.5 \cdot 10^4$ ,  $9.7 \cdot 10^4$ ,  $5.6 \cdot 10^4$ ,  $2.3 \cdot 10^4$  cycles for 1.61, 2.8, 4.9 and 15 % DSA, respectively. It is worth noting that the maximum value of  $E'$  reached at the end of step 2 is higher than that observed at the beginning of the test, thus meaning that the material becomes stiffer than in its initial state. Step 3 corresponds to a decrease



**FIGURE 2.** ELEMENTARY STEPS OF A FATIGUE TEST ILLUSTRATED AT 2.8 % DSA AT AMBIENT TEMPERATURE



**FIGURE 4.**  $\tan(\delta)$  vs. THE NUMBER OF CYCLES AT AMBIENT TEMPERATURE FOR THE FOUR DSA CONSIDERED



**FIGURE 3.** MAGNIFIED VIEW OF  $E'$  ON THE FIRST THOUSANDS OF CYCLES REALISED AT AMBIENT TEMPERATURE FOR THE FOUR DSA CONSIDERED.

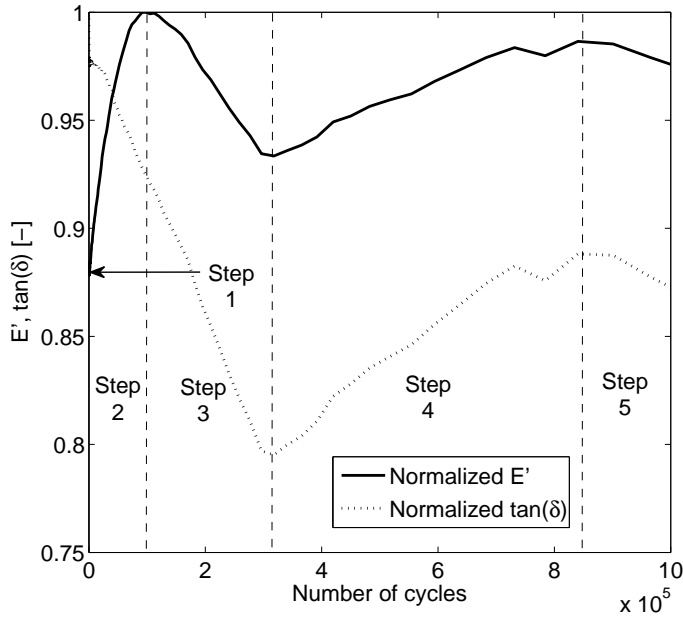
in  $E'$ . It is longer than step 2. Step 4 corresponds to an increase in  $E'$ . It is longer than step 3. Figure 2 shows that the material hardening rate during step 4 is lower than both the softening rate during step 3 and the hardening rate during step 2. Finally, step 5 corresponds to a decrease in  $E'$ . The limits of the steps in terms of number of cycles depend on the DSA.

These results clearly illustrate the complexity of the mechanical response of the filled nitrile under cyclic loading. This emphasizes the fact that the material is subjected to both physical and chemical evolutions at the same time. With classic DMTA,

the viscoelastic response of rubber depends on the cyclic disruption and reformation of the filler network, as well as on the possible release of occluded rubber [10]. Under fatigue, some additional phenomena occur such as fatigue of the filler network and chemical evolutions of the rubber matrix (for instance vulcanization, chains scissions [13]).

Figure 5 is now used in order to discuss the mechanisms involved during the five steps which are clearly bounded. For steps 1, 3, 4 and 5, the variation of the loss factor is similar to that of  $E'$ , *i.e.* the viscosity increases as  $E'$  increases, and then decreases as  $E'$  decreases.

Step 2 is now considered again for comparison purposes with step 4. Similarly to step 4, step 2 corresponds to material hardening, but while the loss factor increases during step 4, either it begins to increase before decreasing during step 2 (for 1.61 and 4.9 % DSA) or it first slowly decreases, and then more quickly (for 2.8 and 15 % DSA) decreases. This is clearly visible in Fig. 5 where both the normalized values of  $E'$  and  $\tan(\delta)$  are represented: during steps 2 and 3,  $\tan(\delta)$  regularly decreases while  $E'$  increases and then decreases during step 3. On the contrary, during step 4, both  $E'$  and  $\tan(\delta)$  increase. This illustrates that the hardening mechanism is different for steps 2 and 4. As mentioned above,  $E'$  significantly increases during step 2. This can be explained by several scenarios. The first scenario is that this increase in  $E'$  can be attributed to the vulcanization of the rubber matrix. However,  $\tan(\delta)$  still decreases in step 3, and  $E'$  should continue to increase instead of decreasing. Consequently, the authors believe that this scenario is not the most realistic. Another explanation is the influence of the reinforcing fillers on the

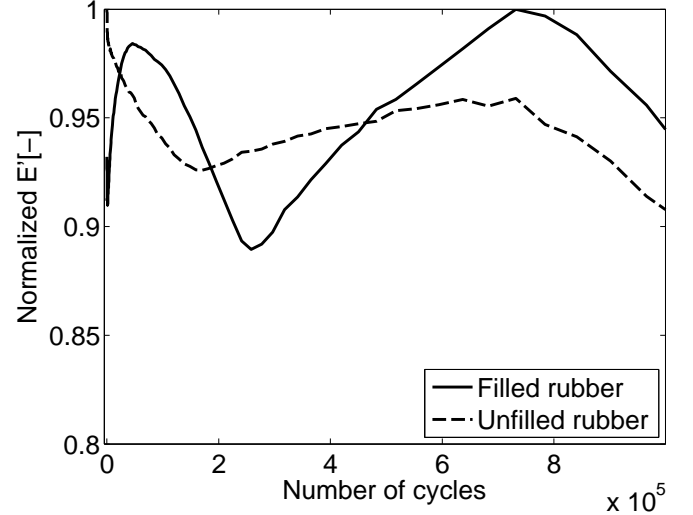


**FIGURE 5.** SUPERIMPOSITION OF NORMALIZED  $E'$  AND  $\tan(\delta)$  FOR 2.8 % DSA AT AMBIENT TEMPERATURE

mechanical response of the material. To shed light on the cause of the phenomenon, one of the experiments described above was performed on an unfilled rubber specimen. A higher DSA was used (15 % DSA), to try to reflect the fact that macromolecules sustain a local stress level. This stress level is certainly significantly higher than that sustained by the macromolecules in the unfilled material, because fillers act as local stress concentrators in the filled material [14]. Figure 6 compares the responses of a filled and an unfilled rubber specimen. It clearly appears that the response of the unfilled rubber specimen is not the same as that of the filled one, since  $E'$  continuously decreases up to  $1.7 \cdot 10^5$  cycles for the unfilled material only. Therefore it is possible to conclude that the fillers are the cause of the phenomenon discussed above. To the best of the authors' knowledge, this phenomenon concerning cyclic loading with low DSA has not been reported in the literature until now. Finally, similar results can be observed concerning the variation in the normalized value of  $E'$  at higher numbers of cycles. The fact that the normalized value of  $E'$  increases, and then decreases, may be due to the macromolecular network. It is clear that it can be due neither to the filler network nor to its interaction with the macromolecular network, since this phenomenon can be observed in both the filled and unfilled rubbers.

It must be emphasized that a stabilized response is generally considered to predict the behaviour of the material at high number of cycles [15, 16]. The current study clearly shows that this assumption might not be accurate enough, because it does not

take into account the microstructural evolution of rubber, at least for the material studied in the present work.



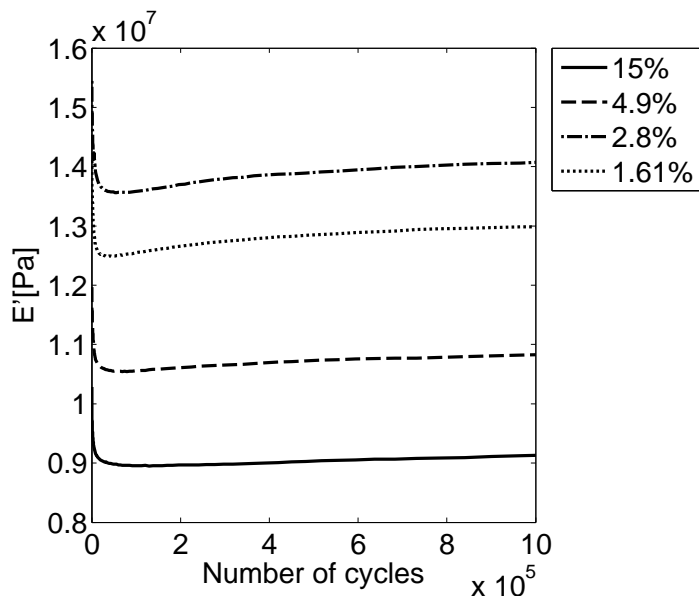
**FIGURE 6.** SUPERIMPOSITION OF NORMALIZED  $E'$  OF FILLED AND UNFILLED NITRILE RUBBER AT AMBIENT TEMPERATURE AT 2.8 AND 15 % DSA RESPECTIVELY

### Cyclic loading tests at 80 °C

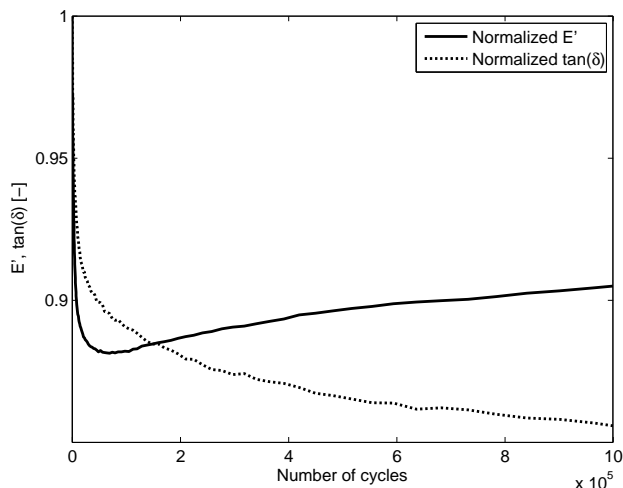
The effect of the temperature on the viscoelastic response of filled nitrile rubber under cyclic loading is investigated in the current section. The previously described tests were performed at 80 °C for this purpose.

Figure 7 gives the variation in  $E'$  during the tests. The curves observed in this case are simpler than those obtained at ambient temperature. First, each curve exhibits the same global shape. Second, the viscoelastic response can be split into two steps. The first step corresponds to a strong decrease in  $E'$  during the first  $5 \cdot 10^4$  cycles. This is due to the combination of the material softening, which is a well-known phenomenon, and viscosity. Then, during the second step,  $E'$  slightly and continuously increases.

Figure 8 shows a superimposition of the normalized value of  $E'$  and  $\tan(\delta)$  vs. the number of cycles for 4.9 % DSA.  $\tan(\delta)$  continuously decreases, first significantly during the first step and then slightly during the second step. The fact that  $E'$  increases and  $\tan(\delta)$  decreases during the second step tends to show that the material is subjected to vulcanization. As a high temperature tends to reduce the effect of fillers, the fact that an increase in  $E'$  is not observed during the first thousand cycles confirms that step 2 in Fig. 5 is due to fillers.



**FIGURE 7.**  $E'$  vs. THE NUMBER OF CYCLES AT 80 °C

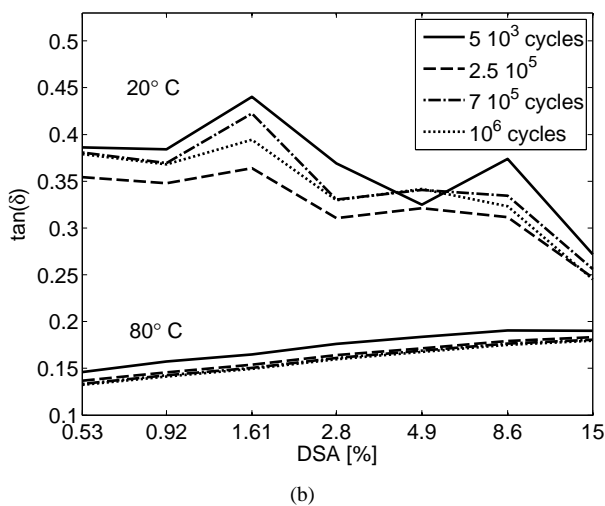
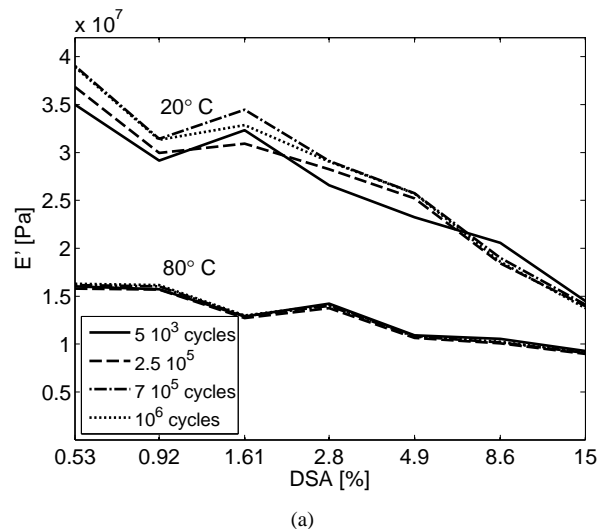


**FIGURE 8.** NORMALIZED  $\tan(\delta)$  AND  $E'$  FOR 4.9 % DSA AT 80 °C

### Influence of the number of cycles on the Payne effect

In the previous sections, the evolution of certain mechanical quantities, *viz.*  $E'$  and  $\tan(\delta)$ , was given *vs.* the number of cycles. The Payne effect is classically represented in the  $E'$ -DSA diagram. Various curves showing the variation in  $E'$  and  $\tan(\delta)$  *vs.* the DSA are therefore plotted at different stages of the tests to characterize and discuss the influence of the number of cycles on the Payne effect. These curves are plotted for both the ambient temperature and 80 °C.

Figure 9 shows some  $E'$ -DSA curves obtained for various



**FIGURE 9.**  $E'$  (A) AND  $\tan(\delta)$  (B) OF FILLED NITRILE RUBBER *vs.* DSA FOR DIFFERENT NUMBER OF CYCLES AT BOTH AMBIENT TEMPERATURE AND 80 °C USING COMPRESSIVE LOADING

numbers of cycles. Four values of the number of cycles have been chosen:  $5 \cdot 10^3$ ,  $2.5 \cdot 10^5$ ,  $7 \cdot 10^5$  and  $10^6$  cycles. The following comments can be made.

First, for both temperatures, the number of cycles does not modify the global curve shape. This may indicate that the Payne effect is not altered by the number of cycles or the temperature.

Due to the fact that the step duration is different for each DSA level, it is difficult to compare quantitatively the relative position of the curves. Nevertheless, it clearly appears that at ambient temperature, the gap between the curves observed for low DSA levels is greater than for higher DSA. These curves tend to the same value at 15 % DSA. This means that the higher the DSA level, the lower the influence of the number of cycles.

Indeed, at high DSA the filler network no longer has any influence on the mechanical response. At 80 °C, this phenomenon is not observed any more and the curves are superimposed. As observed during classic DMTA, DSA has only a small effect on  $E'$ . This is certainly the reason why no difference is observed between the curves for different numbers of cycles.

## CONCLUSION

The effect of cyclic loading on the viscoelastic properties of filled and unfilled nitrile rubbers is addressed in this study.

Classic DMTA has confirmed that the viscoelastic response of the filled nitrile rubber under study submitted to tensile and compressive loading conditions exhibits features previously reported in the literature.

The following conclusions can be drawn from the cyclic tests performed for several DSA at both ambient temperature and 80 °C:

1. the viscoelastic properties of the filled rubber clearly evolve during the cyclic loading tests;
2. in filled nitrile rubber, at ambient temperature and after the stress softening step,  $E'$  is greater than its initial value, apart from the highest DSA. This phenomenon is not observed in unfilled nitrile. This tends to prove that it is caused by the filler network;
3. at 80 °C and for each DSA,  $E'$  slowly increases after a short softening phase. This is observed until the end of the test. This increase in stiffness seems to reveal a progressive vulcanization of the filled rubber;
4. The Payne effect is not really modified, even from a quantitative point of view, by the number of cycles.

The first two points should be taken into account for a better prediction of variations in viscoelastic behaviour during cyclic loading. Further work in this field is currently being carried out by the authors.

## ACKNOWLEDGMENT

The PCM Company is acknowledged for its financial support. The authors are also very grateful to Dr Berton, Mrs Serres, M Perret, M Chatelain and M Fay for fruitful discussions.

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