ELIMINATION OF THE MULLINS EFFECT FOR FOUR RUBBERS

Elli Gkouti^{1*}, Burak Yenigun^{1**}, Aleksander Czekanski^{1***}

¹Department of Mechanical Engineering, Lassonde School of Engineering, York University, Toronto, ON, Canada *gkoutiel@yorku.ca, **byenigun@ yorku.ca, ***alex.czekanski@lassonde.yorku.ca

Abstract—Rubbers constitute commonly used materials for engineering application, such as dumpers, due to their unique physical and chemical properties. However, the proper application of rubbers to specific conditions requires a careful examination of their viscoelastic behavior. An important factor to be considered is the stress softening that rubbers exhibit during the cycle following the initial loading, known as Mullins effect. This phenomenon is extremely significant as the stress value used for reaching a specific strain value might be overestimated. Mullins effect varies for different rubbers and conditions, depending in several factors such as the consistency of the rubber (filled or not), strain value, speed, temperature, etc. In the current research four different rubbers are subjected to 12 cycle loadings for two different speeds.

Keywords-rubbers; Mullins effect; stress softening; preconditioning; viscoelasticity;

I. INTRODUCTION

For understanding and hence, simulating elastomers' viscoelastic behavior, the phenomenon of stress softening is mandatory to be examined and understood in detailed. The past decades, several researchers deal with this phenomenon which refers to the significant change rubbers behavior when they are subjected to repeating extension. Moreover, this change is more obvious on the unloading, which follows the virgin loading. This phenomenon was first observed by Bouasse and Carriere [1], but deeper research has been done by Mullins [2]. At the beginning, Mullins conclude that this phenomenon affects only filled natural rubbers, as their softening was aroused by the increasing stiffening ability. A few years later, he realized that pure natural rubbers conjure stress softening as well [3,4]. It is obvious that several factors affect the stress softening phenomenon, as it is a damage procedure that occurs in the molecules' chains. Apart from materials whose consistency vary, some other factors are related to temperature, strain value or speed that the crosshead is moving in order to deform the griped sample [5-7].

From then, this phenomenon remains a challenge as it is necessary to be deeply understood, for simulating and predicting the mechanical behavior of rubbers. The most selected approach of describing Mullins effect is related to the damage continuum mechanics. Specifically, the material is treated as hyperelastic and the strain energy density function is converted for including a damage parameter. Based on the above idea, Ogden and Roxburgh [8] have introduced a pseudo-elastic model for accounting stress softening of rubbers. Additionally, the way to eliminate the Mullins effect is to perform several loading-unloading cycles before we start the experimental test that we desire, a procedure that is also known as preconditioning. According to Dorfmann and Ogden [9], after six loading cycles the required stress for loading-reloading converges almost to the same value.

In the present work, we recorded that 6 cycles might not be enough for some rubbers in order to eliminate the stress softening. Hence, four elastomers with different consistency, namely natural rubber, silicone rubber, Neoprene and EPDM, were subjected to large deformation for 12 cycles of loading and unloading. Moreover, the decreasing amount of stress that is required for each rubber to be reached, the desired strain value varies for different speeds of the crosshead. Hence, we repeated the above experimental tests for a higher speed. In the following section of the current work, we give a brief explanation of the Mullins effect and also, the experimental procedure that we followed. In the third section, results are shown of describing this phenomenon and then, some useful conclusions are obtained.

II. EXPERIMENTAL PROCEDURE

A. Mullins Effect

A phenomenon associated with stress softening, the Mullins effect, must be accounted for to meet the requirements of the present research [2, 4, 6, 8]. Namely, when a rubber sample is extended from its virgin position, unloaded, and then reloaded again, the required stress upon reloading is less than that needed at the first loading for strains up to the maximum strain reached on the initial loading. After some cycles, the stress level is observed to reach an almost constant value [4].

B. Experimental Investigation of the Stress Softening Phenomenon

In order to capture the phenomenon of stress softening between the primary and following cycles, we selected four representative elastomeric materials, natural rubber, silicone, Neoprene and EPDM [X]. For each of the above rubbers, we cut coupons in a so-called dog-bone shape (115mm x 25mm x 3.175mm). The experimental procedure begun by subjecting each sample to uniaxial tension until it reached 100% of strain which is considered to be a large deformation. Then the unloading followed until 20% of the maximum strain was reached. We selected to examine these rubbers by leaving a residual strain during unloading in order to avoid folding of the samples. We repeated the above 11 cycles more and the relationship between stress-strain was recorded. The experimental tests were performed in an MTS machine, where the speed of the moving crosshead was 0.1mm/s.

In previous work the effect of the strain value was studied and several results were obtained that prove the dependency of the Mullins effect with the deformation that the material is subjected [X]. In the current paper, we want to show the effect of the speed as well. Hence, we repeated the procedure for a higher speed, meaning 1mm/s and the results are shown in Fig. 2. We should mention that all experimental tests were performed at the temperature of 23° C.

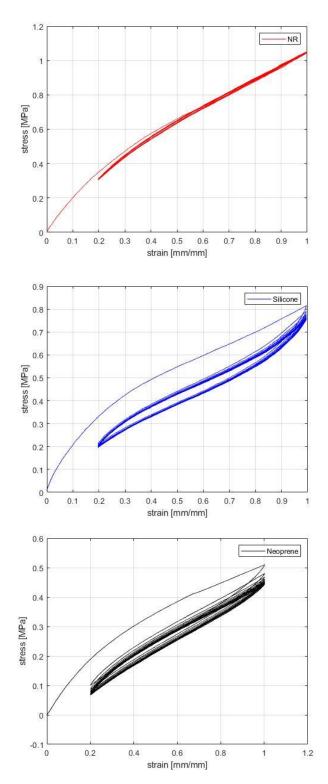
III. RESULTS AND DISCUSSION

Fig. 1-2 show the Mullins effect that occurs in the samples of four different rubbers for 0.1mm/s and 1mm/s speed, respectively. A significant result is that the maximum softening of all cycles, always appears during the reloading after the primary extension. In the following cycles, softening reduces depending in the material that the rubber is made. For more filled materials such as EPDM or Silicone, the softening almost eliminates after the 10th and 8th cycle, respectively, while Neoprene after the 6th cycle. Natural Rubber is obviously the material that is merely affected by stress softening during reloading due to the fact that is considered to be an unfilled rubber. Consequently, its stress values do not conjure huge variations. After the 1st cycle the stress value can be used for accurate models and simulating results. The acknowledgement that Ogden and Roxburgh [8] made in the past, namely that 6 cycles are necessary for eliminating the stress softening is debatable.

Furthermore, the speed that the crosshead is moving in order to deform the sample adequately affects the required amount of stress in every cycle. In Fig. 1-2, the comparison between 0.1mm/s and 1mm/s show that the stress value is increased for higher speed and the softening occurs in a greater degree. Specially for natural rubber, we can observe that the initial with the following loading exhibit a countable decrease for 1mm/s, while in the lower case the cycles almost coincide. For Silicone and EPDM, we can observe the greatest difference between the speeds 0.1mm/s and 1mm/s since stress softening occurs the sample for several loading cycles.

IV. CONCLUSIONS

Mullins effect is observed in several experimental procedures where rubbers are subjected to repeated uniaxial tension until the desired strain level is achieved. The stress softening occurs more for rubbers such as Silicone, Neoprene and EPDM as well as for higher speeds. As a result, preconditioning of the samples is mandatory before the actual experimental tests begins. In contrast to past acknowledgement elastomers must be examined for several repeating cycles, even more than six, for reassuring that the phenomenon almost vanishes and so accurate simulations and predictions can be achieved.



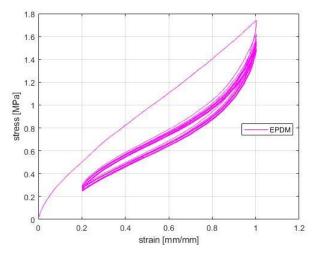
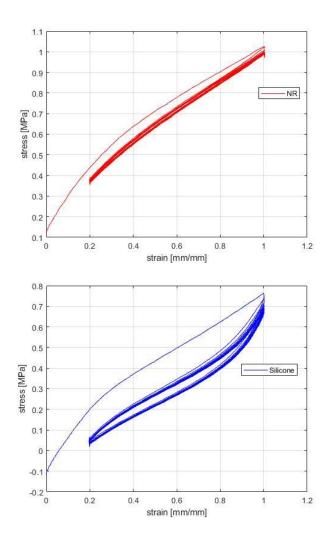


Figure 1. Natural Rubber, Silicone, Neoprene, EPDM subjected to 12 loading-unloading cycles until 100% strain for 0.1mm/s speed at 23oC.



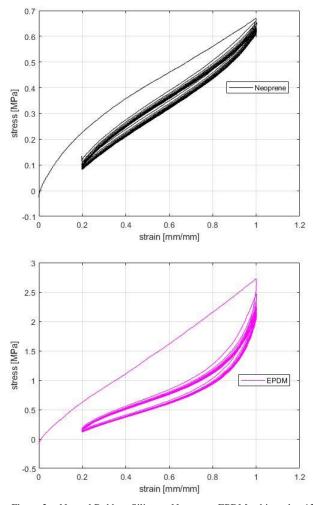


Figure 2. Natural Rubber, Silicone, Neoprene, EPDM subjected to 12 loading-unloading cycles until 100% strain for 1mm/s speed at 23oC.

REFERENCES

- [1] H. Bouasse and Z. Carriere, "Courbes de traction du caoutchouc vulcanise," Ann. Fac. Sci.Toulouse, vol. 5, pp. 257-83, 1903.
- [2] I. Mullins, "Effect of stretching on the properties of rubber," J. Rubber Res., vol. 16, pp. 275-82, 1948.
- [3] I. Mullins and N.R. Tobin, "Theoretical model for elastic behavior of filler reinforced vulcanized rubbers," Rubber Chem. Technol., pp. 55-71, 1957.
- [4] I. Mullins, "Softening of rubber by deformation," Rubber Chem. Technol., vol. 42, pp. 339-62, 1969.
- [5] F. Bueche, "Mullins effect and rubber-filler interaction," Journal of Applied Polymer Science, vol. V(15), pp. 271-281, 1961.
- [6] E. Gkouti, B. Yenigun and A. Czekanski, "Transient effect of applying and removing strain on the mechanical behavior of rubber," Materials, vol. 13, pp. 4333, 2020.
- [7] E. Gkouti, B. Yenigun, K. Jankowski and A. Czekanski, "Experimental study of Mullins effect in natural rubber for different stretch conditions," Proceeding of the ASME 2020, International Design Engineering Technical Conferences and Computers and Informatio in Engineering Conference IDETC/CIE2020, Virtual, Online, August 17-19, 2020.

- [8] R.W. Ogden and D.G. Roxburgh, "A pseudo-elastic model for the Mullins effect in filled rubber," Proc. R. Soc. London A, vol. 455, pp. 2861-77, 1999.
- [9] A. Dorfmann and R.W. Ogden, "A constitutive model for the Mullins effect with permanent set in particle-reinforced rubber," Int.. J. Solids Struct., vol. 41, pp. 1855-78, 2004.