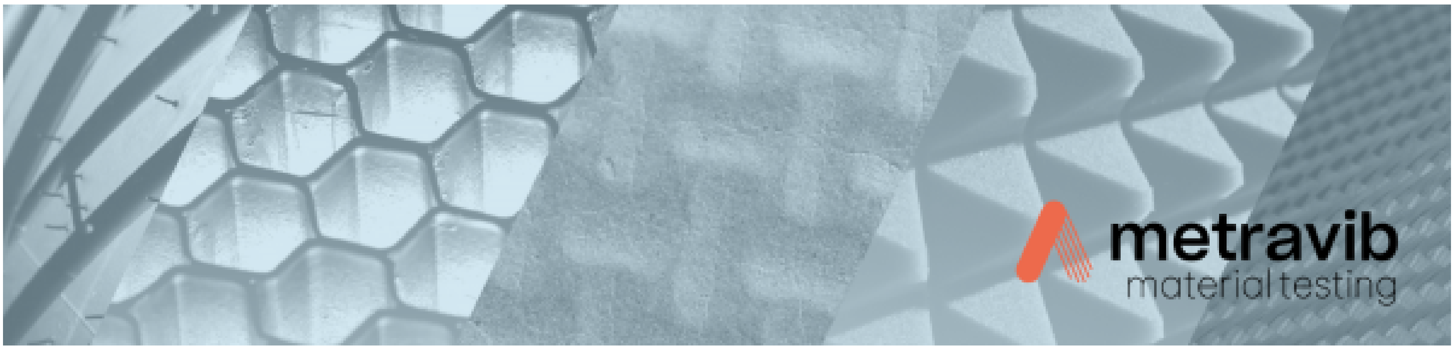


Mullins Effect

Keywords: DMA, Glass Transition, Viscoelasticity, Large-scale deformations, Elastomers, Mullins effect

Figure 1. Metravib DMA+1000.

Introduction

A viscoelastic material subjected to a strain rate sweep exhibits two distinct behaviors (see diagram below):

- linear behavior or linear zone (for which Hooke's law is verified); zone in which modulus and Tan δ are constant.
- a non-linear behavior or non-linear zone in which the E' modulus decreases as a function of the rate of deformation, and a Tan Delta peak can be observed.

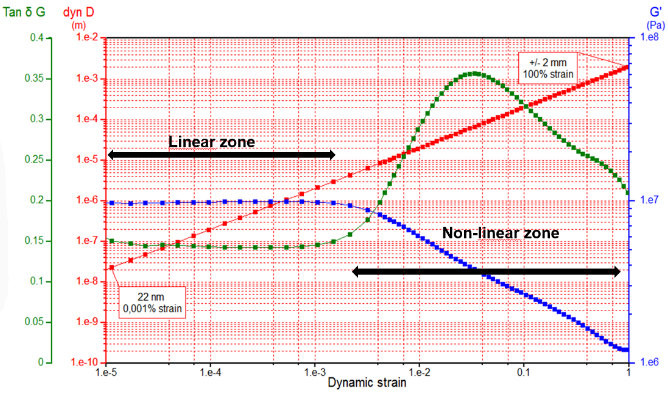


Figure 2. Strain rate sweep on an elastomer in shear mode.

From this measurement, Mullins effect can be studied [1].

Mullins Effect

The Mullins effect is a phenomenon that can be observed when increasing strain cycles are applied to an elastomer material. Theoretically, the first deformation cycle leads to irreversible (or kinetically slow) modifications in the polymer chains. As a result, the modulus (E or G) of the polymer decreases for equivalent deformation levels, and this effect can be observed when several successive deformation cycles are applied to a specimen. In other words, the Mullins effect can be summed up as a reduction in modulus attributed to a reduction in the number of effective elastic chains in the network. It should be noted that the Mullins effect can be partially reversible over long periods at room temperature, or by changing temperature[3].

The Mullins effect has several explanations:

- Breakage of charge aggregates or charge-matrix bonds;
- Breaking of weak charge-polymer bonds;
- Breakage of chains of different lengths between adjacent loads;
- Deformation-induced sliding of elastomer chains adsorbed to filler surfaces.

This study shows the effect of large-scale deformations on elastomers in terms of Mullins effect. It also shows the capability of Metravib DMA range, to characterize materials viscoelastic properties even in non-linear zone to identify the effects such as Mullins effect.

Materials & methods

The material used for this study was filled rubber. The specimens used for this study were 2 mm thick with 10 mm diameter. The specimens were studied in shear mode Figure (3). The dynamic strain sweep performed from 0,003% to 160% of deformation was applied on the specimen at 10 Hz.

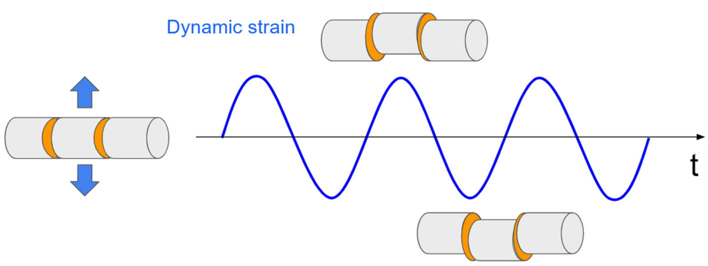
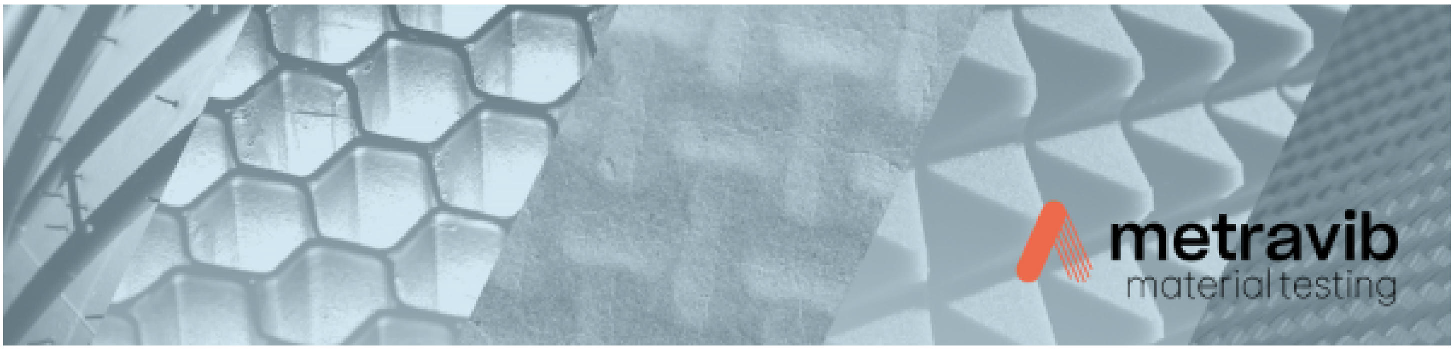


Figure 3. Schematic diagram of Shear test mode

The parameters used for the test are mentioned in Table 1.



Dynamic Strain	3e-5 to 1.6 then 1.6 to 3e-5
Frequency (Hz)	10
Temperature (˚C)	Room temperature
DMA	DMA+1000
Test Mode	Shear

Table 1. Test parameters

Results

Figure 4 shows the results obtained for the strain sweep at 10 Hz.

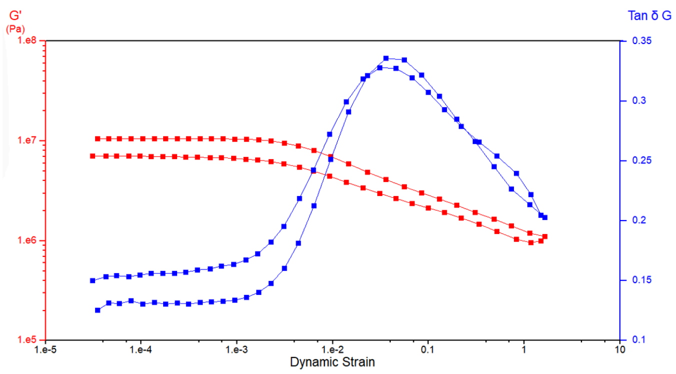


Figure 4. G' and tan δ as a function of dynamic strain at 10 Hz.

The linear viscoelastic region was observed to be until 0,2% for this rubber specimen. As the specimen went out of linear viscoelastic region as a result of large-scale deformation, it was observed that the viscoelastic properties i.e., the shear storage modulus (G') decreased when the applied strain sweep came back to the minimum strain applied (drop of around 30%). This drop is representative of the Mullins effect in the rubber material.

Several descriptions can be suggested to explain this phenomenon in rubber materials. These descriptions include chain breakage at the interface between the rubber and the fillers, slipping of molecules, rupture of the clusters of fillers, chain disentanglement, to form a more complex composite structure [3].

Conclusions

This study was performed to understand the effect of large-scale deformations on rubber like materials. The strain sweep and reverse strain sweep have shown the irreversible damages caused by the high strain values. This phenomenon goes with the residual strain and induced anisotropy. This phenomenon is attributed to several explanations such as chain breakage at the filler-rubber interface, slipping of molecules, rupture of the clusters of fillers etc.

Knowing the importance of this phenomenon, it is important to characterize these types of rubbers as it could be a key information for the rubber manufacturers, especially in the tire industry.

This study also shows the unrivaled capabilities of Metravib DMA series of applying large-scale deformations on such materials.

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