Stress relaxation, stress recovery and stress memory in filled EPDM rubber

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Abstract

Although the magnitude of inelastic and viscoelastic effects in filled rubbers is small relative to the elastic response, these effects are nevertheless critical in several applications such as gaskets and dampers. The purpose of this study is to investigate the role of deformation history, and hence of the Mullins effect, on viscoelasticity of rubber through time-dependent experiments. Cross-linked filled EPDM rubber is subjected to a range of uniaxial deformation histories followed by stress-relaxation or stress memory at fixed deformation. Stress relaxation is affected by deformation history in a similar way to the constitutive response. Stress memory following a load-unload cycle is instead independent of deformation history. The experiments confirm that deformation history has a significant role to play in determining the time-dependent response of rubber.

Keywords: Viscoelasticity, Mullins effect, EPDM, time-dependence, stress memory, stress relaxation.

Introduction

Elastomers are best known for their ability to undergo large elastic deformations, but there are many applications whose performance is dictated by the magnitude of inelastic and viscoelastic effects. For example, seals and gaskets are frequently evaluated in terms of compression set,[1] which is itself a time-dependent phenomenon. Although the precise behaviour is influenced by aspects such as choice of formulation and curing, to the authors' knowledge there is no comprehensive study of the role of deformation history on viscoelasticity of elastomers in the literature. Limited elastomer experimental data is available on short-term stress relaxation of chloroprene and natural rubbers,[2] and of thermoplastic polyurethane elastomers,[3] but none of these studies explore more complex load histories. The effect of deformation history is perhaps best known through its manifestation as the softening phenomenon known as the Mullins effect,[4, 5] where the deformation itself causes (semi) permanent changes in the microstructure, and hence in the mechanical response.[2, 6] Thus, it is plausible to expect that the inelastic and viscoelastic response of a given rubber may be unavoidably and intrinsically connected with the Mullins effect.

In this paper we employ a methodology inspired by the recent work of Caruthers and co-workers on polymer glasses[7] and carry out a series of short term stress-relaxation experiments on rubber subjected to a wide array of prior deformation histories in order to shed light on this relatively unexplored phenomenon. The objective is to contribute to the body of knowledge necessary for a fully time- and history-dependent constitutive model of rubber deformation.

Experimental methods and materials

Cross-linked carbon black filled (50phr) oil extended ethylene-propylene-diene rubber (EPDM) was used throughout this work. Sheets ~0.5 mm thick were cross-linked by compression moulding using a heated press at 160°C for 13 min. Specimens for uniaxial tensile testing were cut to ~10 mm width using a sharp bladed cutter. Individual specimen thickness was recorded using a rubber thickness gauge (Hildebrand ISO 23529), and width using a calibrated scanner system.

Uniaxial mechanical deformation was carried out using an Instron model 5969 tensile testing machine equipped with 50kN load cell and an Instron travelling extensometer. All tests were performed at room temperature (20±1°C) at a constant nominal strain rate of 0.1 s^{-1}. In order to study the influence of deformation history on stress relaxation, four test protocols (TPs) were applied prior to recording stress relaxation at fixed displacement for a further 600 s:

- TP1. Specimens subjected to a single loading ramp through to strains ranging between 50% and 200%, as shown in the inset of Fig. 2a.
- TP2. Specimens subjected to a single load-unload cycle to maximum strains of 100%, 150% and 200%, unloading to 0.1 N, followed by a single loading ramp through to strains ranging between 50% and 200% as shown in the inset of Fig. 2b.
- TP3. Specimens subjected to a single load-unload cycle to maximum strains between 50% and 200%, unloading to 0.1 N (to prevent buckling), as shown in the inset of Fig. 4a.
- TP4. Specimens subjected to a single loading ramp through to 200% strain, unloaded to strains ranging between 175% and 50%, as shown in the inset of Fig. 4b.

Typical stress-strain curves illustrating the points at which stress-relaxation measurements were started are shown in Fig. 1. Nominal stress is reported throughout.

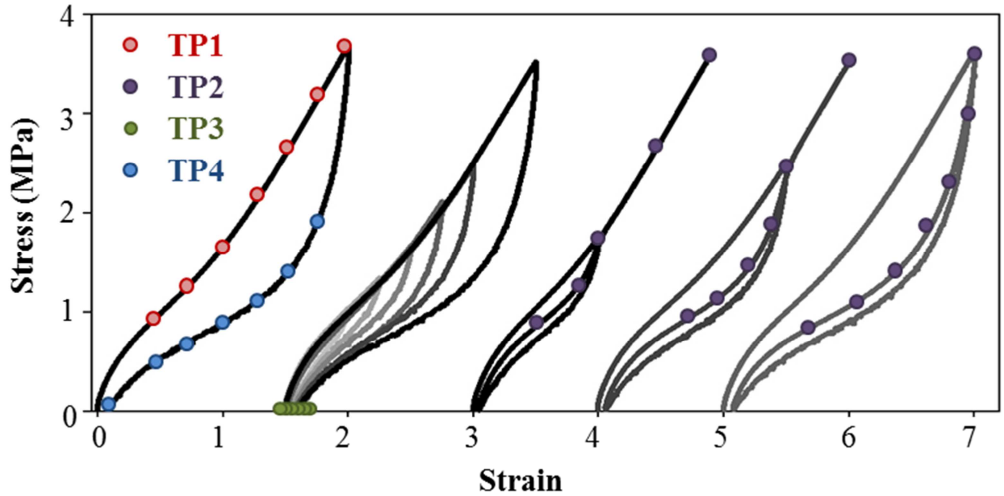

Fig1. Nominal stress measured as a function of strain for EPDM specimens deformed according to TP1, TP4, TP3 (offset by 1.5), and TP2 (offset by 3,4 and 5 respectively). Circles indicate the start of the stress relaxation measurements.

Results and discussion

Dependence of stress relaxation on deformation history

The stress relaxation of specimens subjected to TP1 is shown in Fig. 2a, normalised by the stress at the end of the loading ramp, σ_{end}. The response is significantly dependent on strain history: a bigger fraction of the stress relaxes after loading to larger strains. Fig. 2b shows stress relaxation of specimens subjected to TP2, which includes a prior load-unload cycle through to 200%. The stress relaxation response differs clearly from that of Fig. 1a, with all specimens relaxing a smaller fraction of the stress than their counterparts from TP1. Surprisingly, specimens deformed to strains of 50% - 150% relax an almost identical *fraction* of the stress, around 6% in 600 s, even though the magnitude of σ_{end} (see Fig. 1) differs significantly. Only when reloading close to the original maximum strain does the relaxation fraction increase beyond 6%.

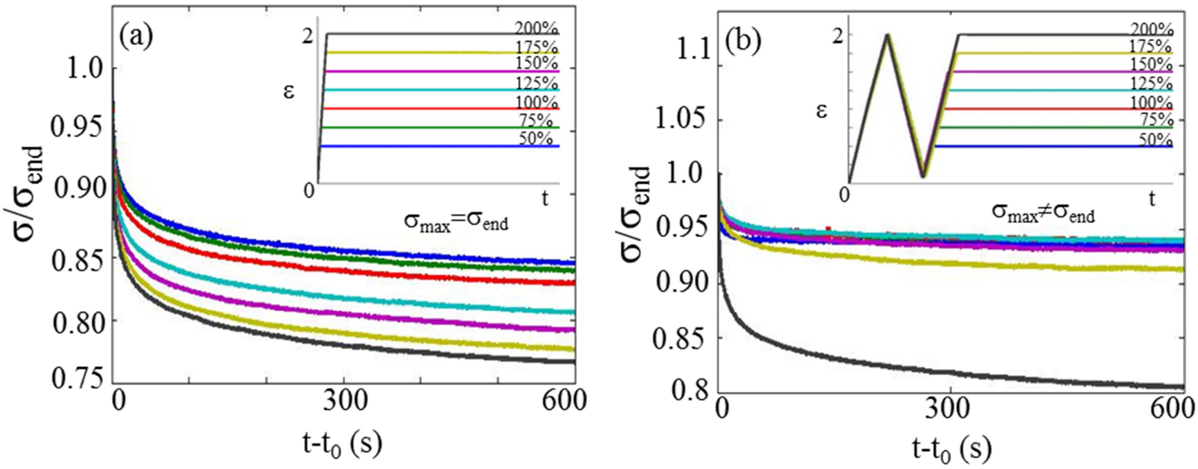

Fig. 2 (a) Normalised stress relaxation σ / σ_{end} of EPDM specimens subjected to TP1 deformation histories (inset); (b) normalised stress relaxation of EPDM specimens subjected to TP2 deformation histories (inset). t_0 is the time at the start of the stress-relaxation.

The fraction of unrelaxed stress at 600 s, $\sigma_{r,600} / \sigma_{end}$, is plotted as a function of the strain at the end of the experiment in Fig. 3, for the experiments described above, and for additional tests according to TP2 but with the load-unload cycle through to 100% and 150% strain. The data shows a distinctive pattern. Where stress relaxation follows only a loading ramp, the unrelaxed fraction is lower, ranging between 0.76-0.85. Specimens loaded, unloaded and reloaded to strains smaller than the previous maximum produce an approximately constant fraction of unrelaxed stress of ~0.94. Specimens loaded, unloaded and reloaded to strains equal to or larger than the previous maximum instead converge towards the lower fraction. Hence, deformation history, and hence the Mullins effect, is shown to affect the fraction of unrelaxed stress much in the same way as it affects the stress-strain response. This aspect is important in the design of elastomeric products such as seals where variations in the applied strain can cause a deviation in the time-dependent stress response, and in the elastic fraction, potentially compromising the performance.

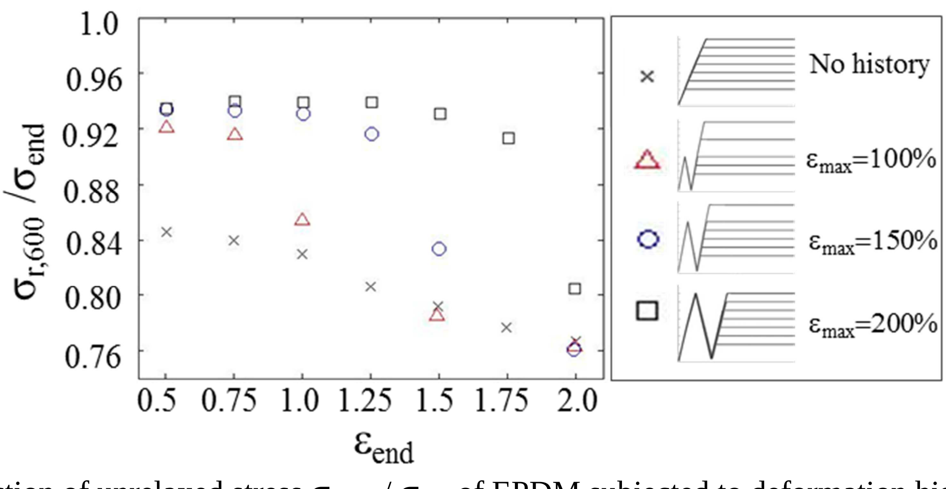

Fig. 3 Fraction of unrelaxed stress $\sigma_{r,600} / \sigma_{end}$ of EPDM subjected to deformation histories TP1 and TP2 to varying levels of maximum deformation ε_{max} and final deformation ε_{end} (inset on the right).

Dependence of stress memory on deformation history

The recovery of stress following a load-unload cycle to strains ranging from 50% to 200% according to TP3, termed stress memory, is shown in Fig. 4a. The stress memory, and the value of stress after 600 s is remarkably similar for all specimens, and appears approximately independent of the deformation history, and of the fact that specimens experienced dramatically differing stresses during the load-unload cycle (see Fig.1). This is in sharp contrast with the dependence of stress relaxation on history observed in TP1 and TP2. Stress memory of this kind could be attributed to a simple, non-hysteretic viscoelastic mechanism.

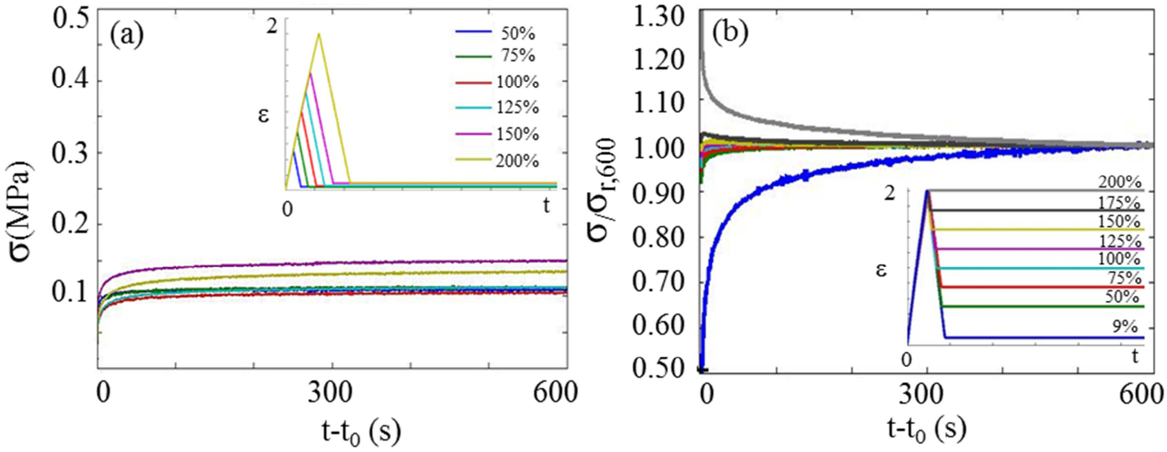

Fig. 4 (a) Stress recovery (memory) as a function of time for EPDM specimens subjected to deformation histories according to TP3 (inset), and (b) for specimens subjected to histories according to TP4 (inset). t_0 is the time at the start of the stress-relaxation.

The time-dependent stress normalised with respect to the stress at the end of the unloading ramp σ_{end} for specimens deformed according to TP4 is shown in Fig. 4(b). Here there is evidence of stress relaxation for unloading between 200% (no unloading) and 125%, and of stress recovery for specimens unloaded to strains between 100% and 50%, and to 0.1 N (corresponding to a strain of ~9%). There is a striking difference relative to the data from TP2 shown in Fig. 2b, where upon reloading to various strains there is always stress relaxation, even at 50% strain, and never stress recovery.

Mechanisms of time dependence

There are several patterns emerging from the data presented, and each of these contributes to shaping the form of constitutive model that would be able to capture the observed time- and history-dependence. It appears that although there is a small deformation history-independent viscoelastic component when the material is unloaded, rubber under load exhibits a viscoelastic component of the stress which is instead larger and history-dependent. If stretched to a deformation that is within (and not too close to) the maximum previously reached strain, a constant *fraction* of the stress relaxes (~6% after 600 s). A larger fraction relaxes upon first loading, and also when the maximum strain is approached for the second time. This suggests that deformation history, associated with the microstructural changes underpinning the Mullins effect, will have to be accounted for when modelling stress-relaxation in rubber.

Conclusions

This study has presented new experimental measurements of stress-relaxation and stress-recovery in EPDM rubber subjected to a variety of deformation histories in order to elucidate the underlying mechanisms of time-dependence. It was observed that:

- Where stress relaxation follows a simple loading ramp, between 15-24% of the stress relaxes in 600 s, and this fraction is strain-dependent.
- Where stress relaxation follows a loading ramp to a strain smaller than that previously reached, a constant 6% fraction of the stress relaxes, independent of the applied strain.
- Stress memory following load-unload ramps to different strains is independent of the strain history.
- Where stress is recorded over time after partial unloading, either stress relaxation or stress memory is observed, depending on the strain. If instead it is recorded after partial loading, only stress relaxation is observed.

Work is on-going in our laboratory to assemble a time- and history-dependent constitutive model able to represent these phenomena.

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