Viscoelastic deformation of carbon-black filled EPDM

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1. INTRODUCTION

Filled elastomers are important industrial materials because of their unique flexibility and damping properties, and are used in a range of applications such as seals, dampers, transmission belts and automotive tyres.

They exhibit a range of complex phenomena when subjected to repeated loadings:
(1) the stress-softening phenomenon known as the Mullins effect
(2) complex pre-conditioning dependent viscoelasticity from intermolecular and polymer-filler interactions
(3) a small degree of permanent set.

The generation of constitutive models able to accurately predict the mechanical response of such components forms an essential part of their design, and can also contribute to the understanding of the mechanisms underpinning such a response. We present a series of experimental observations aimed at shedding light on these phenomena and at supporting the implementation of a new constitutive model able to capture these features.

2. MATERIALS AND METHODS

The material used in these experiments was an accelerated sulphur cross-linked carbon-black filled (50phr) oil-extended ethylene-propylene-diene (EPDM) rubber.

0.5mm thick sheets were compression-moulded for 13 minutes at 160ºC; dog-bone specimens were then cut from the sheets. Tensile testing was performed using an Instron testing machine at room temperature. Strain was measured by a counterbalanced elastomer extensometer. A constant true strain rate of 0.03 s^{-1} was imposed, as measured in the gauge length of the specimen by the extensometer, using a feedback loop.

The tests consisted of a pre-deformation loading, followed by 3 unload-reload loops, loading to a specified maximum stretch, and unloading to a tensile force of 0.1N to avoid buckling, see Fig.1. A range of 10 maximum stretches from λ = 1.5-6 were used. Representative stress-strain curves are shown in Fig. 2.

Fig. 1

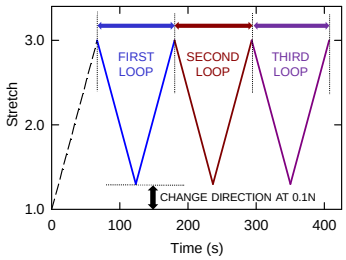
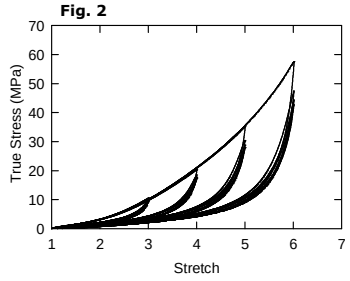


Fig. 2



3. DATA ANALYSIS

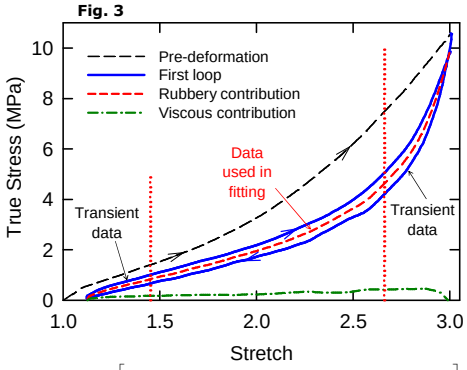
Using the ideas of Haward and Thackray (ref. [1],) two contributions are ascribed to the stress:
(a) an entropy-elastic network with connectivity from chemical cross-links, entanglements and bonding at the rubber-carbon-black interface
(b) viscoelastic inter-molecular interactions.

Unload-reload loops can be used to determine separately the contributions from (a) and (b) (ref. [2]). The network stress is the mean of the unloading and reloading stress at a given strain; the viscous stress is half of the difference between the unloading and reloading stress, see Fig.3. Transients are avoided by eliminating data from the first and final 33% strain of each segment.

The physically based Edwards-Vilgis strain energy function A, shown on the right, is used to model the rubbery contribution in terms of the principal stretches.

Parameters N_s and N_c, the number densities of slip-links and cross-links, α, a measure of finite chain extensibility, and η, the slip-link mobility factor, are fitted using Matlab.
In order to account for the permanent set, λ_{set}=1+ε_{set} is used as a further fitting parameter. The effective stretch λ_{eff} seen by the material after permanent set is related to the measured stretch λ through $\ln \lambda = \ln \lambda_{set} + \ln \lambda_{eff}$.

Fig. 3



$$A = \frac{N_s k_B T}{2}\left[\frac{(1+\eta)(1-\alpha^2)}{1-\alpha^2\sum_{i=1}^{3}\lambda_{set,i}^2}\sum_{i=1}^{3}\frac{\lambda_{set,i}^2}{1+\lambda_{set,i}^2}+\sum_{i=1}^{3}\ln\left(1+\eta\lambda_{set,i}^2\right)+\ln\left(1-\alpha^2\sum_{i=1}^{3}\lambda_{set,i}^2\right)\right]$$

$$+\frac{N_c k_B T}{2}\left[\frac{(1-\alpha^2)}{1-\alpha^2\sum_{i=1}^{3}\lambda_{set,i}^2}\sum_{i=1}^{3}\lambda_{set,i}^2+\ln\left(1-\alpha^2\sum_{i=1}^{3}\lambda_{set,i}^2\right)\right]$$

4. RESULTS

The fitted parameters are shown in Fig.s 4a-d. The rms error in stress remains below 0.5% of the maximum stress for all the loops. Although N_s remains approximately constant with pre-deformation, N_c appears to decrease. The chain inextensibility parameter α is also decreasing. A possible physical interpretation is that, with increasing pre-deformation, some polymer chains are becoming too tightly stretched, and breaking loose from bonding at the polymer carbon-black interface. Thus, there is a reduction in apparent cross-link density, and chains can reach a larger limiting stretch. However, the entanglements (represented by slip-links) are a topological feature of the network and therefore their number density is unaffected by strain.

The entropy-elastic part of the stress, evaluated from the fitted parameters, is shown in Fig.5a. Fig.5b shows the computed viscosity as a function of the effective stretch seen by the rubber. Although the rubber parameters evolve with increasing first deformation, there appears to be a unique viscosity master curve, but with a viscosity that is increasing with increasing stretch.

This implies that the viscous contribution can be represented as a unique function of strain, independent of pre-deformation. The viscous contribution arises from interactions unaffected by breakdown in polymer-filler bonding, but whose flow units are intrinsically anisotropic. With increasing strain, they become increasingly anisotropic as a result of molecular alignment (ref. [4]).

Fig. 5a

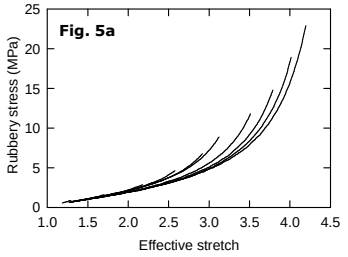


Fig. 4a

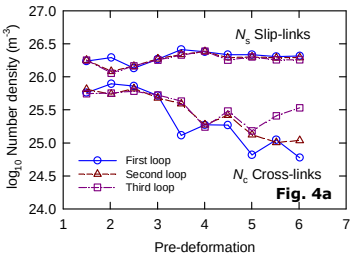


Fig. 4b

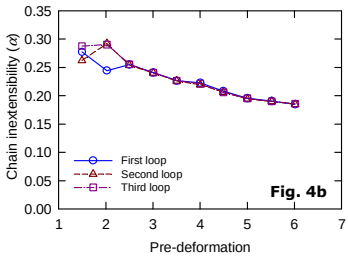


Fig. 4c

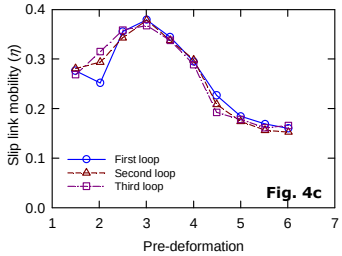
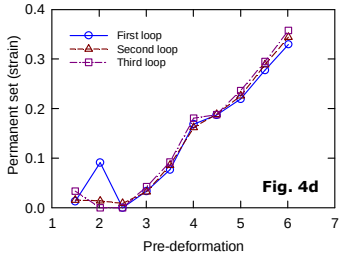


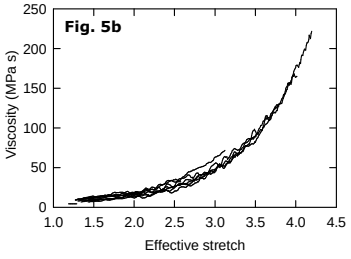
Fig. 4d



5. CONCLUSIONS

The apparent crosslink density reduces with increasing pre-deformation, but the slip-link density remains constant. The viscous contribution is also invariant with respect to pre-deformation, but increases with stretch, possibly revealing increasing anisotropy of flow. This forms a firm basis for the development of a constitutive model able to capture these features.

Fig. 5b



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