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Viscoelastic deformation of carbon-black filled EPDM rubber

Davide S.A. De Focatiis[1,2], Frank Abraham[3] and C. Paul Buckley[2]

[1]*Department of Chemical and Environmental Engineering, University of Nottingham, UK*
[2]*Department of Engineering Science, University of Oxford, UK*
[3]*Mechanical & Design Engineering, University of Portsmouth, UK*
davide.de.focatiis@nottingham.ac.uk; frank.abraham@port.ac.uk; paul.buckley@eng.ox.ac.uk

Cyclic tensile stress-strain data for a cross-linked EPDM rubber are presented. Data are modeled using the Edwards-Vilgis strain energy function with parameters evolving with the maximum stretch, in parallel with viscoelastic anisotropic flow units. The crosslink density reduces with increasing stretch, but the slip-link density and viscous contribution are invariant.

Introduction

Filled elastomers are increasingly 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; and (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. In this paper 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.

Experimental method

The material studied in this work is an accelerated sulphur cross-linked carbon-black filled (50phr) oil extended ethylene-propylene-diene (EPDM) rubber. Sheets of material approximately 0.5mm thick were compression-moulded for 13 minutes at 160ºC using a heated press. Specimens for tensile testing were cut from the sheet using a dog-bone cutter. Tensile testing was performed in an Instron tensile testing machine fitted with a counterbalanced elastomer extensometer, at room temperature at a constant true strain rate of 0.03 s^{-1}, as measured in the gauge length by the extensometer, using a feedback loop. The tests consisted of 4 load-unload cycles, loading to a specified maximum stretch, and unloading to a tensile force of 0.1N to avoid buckling. A range of 10 maximum stretches from λ = 1.5 to λ = 6 were used. Representative stress-strain curves for four such tests are shown in Figure 1(a).

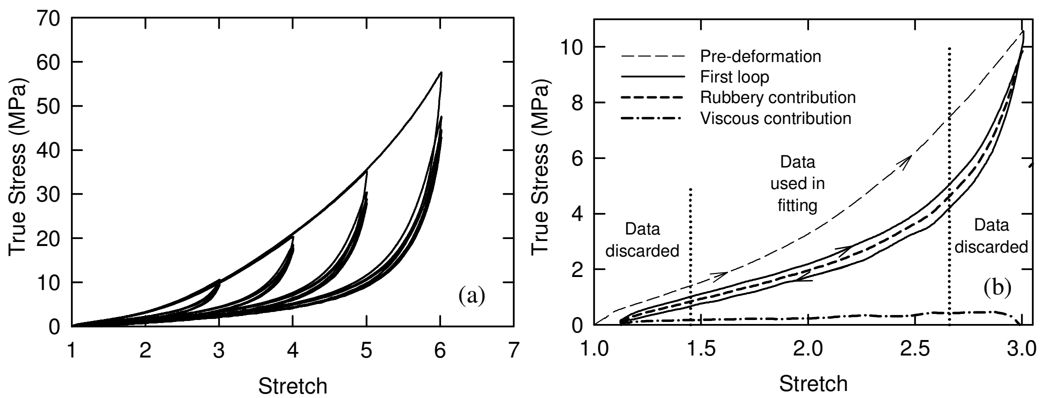

Figure 1 (a) Representative stress-strain cycles to different levels of pre-deformation; (b) the extraction of a rubbery contribution and a viscous contribution from one loop.

Data analysis

The premise for this work is provided by the ideas of Haward and Thackray for the modelling of polymeric materials [1]. Two contributions are ascribed to the stress, arising from (a) an underlying entropy-elastic network with connectivity provided by chemical cross-links (including bonding at the rubber and carbon-black interface) and entanglements, and (b) viscoelastic inter-molecular interactions. The parameters of the network are assumed to depend only on the maximum stretch previously reached. Therefore unloading-reloading loops following the first loading to the maximum stretch can be used to determine separately the contributions from (a) and (b), following a procedure suggested previously [2]. Thus the network stress was calculated as the mean of the unloading and reloading stress at a given strain, and the viscous stress as half of the difference between the unloading and reloading stress, as illustrated in Figure 1(b). In order to remain clear of transients, data from the first and final 33% strain of any loading and unloading cycle is not used for this purpose.

The physically based Edwards-Vilgis (EV) strain energy function [3] was used to model the rubbery contribution, and was implemented in Matlab. An in-house fitting routine was used to find the best set of EV parameters for the rubbery stress obtained from each loop, minimising the rms error in stress. The parameters are N_s and N_c, the number densities of slip-links and cross-links respectively, α, a measure of finite chain extensibility, and η, the slip-link mobility factor. In order to account for the (small amount of) permanent set ε_{set} exhibited by this material, $\lambda_{set} = 1 + \varepsilon_{set}$ is used as a further parameter. Thus the effective stretch λ_{eff} seen by the material after permanent set is related to the measured stretch λ through $\ln \lambda = \ln \lambda_{set} + \ln \lambda_{eff}$.

Results and discussion

The set of fitted parameters N_s and N_c, ε_{set}, α and η are shown in Figures 2(a), 2(b), 3(a) and 3(b) respectively as functions of the maximum pre-deformation. Remarkably, the rms error in stress from the fitting routine remains below 0.5% of the maximum stress in all the loops, indicating that the EV function is appropriate for capturing the particular shape of these curves. There is no significant evolution in the parameters with increasing number of cycles, justifying the assumption that parameters depend only on the maximum stretch previously reached. There is also little strain rate dependence (not shown).

The presence of carbon black in this system leads to a strain amplification in the rubber network. This is at present not specifically accounted for in the parameters N_s, N_c, α, η and ε_{set}.

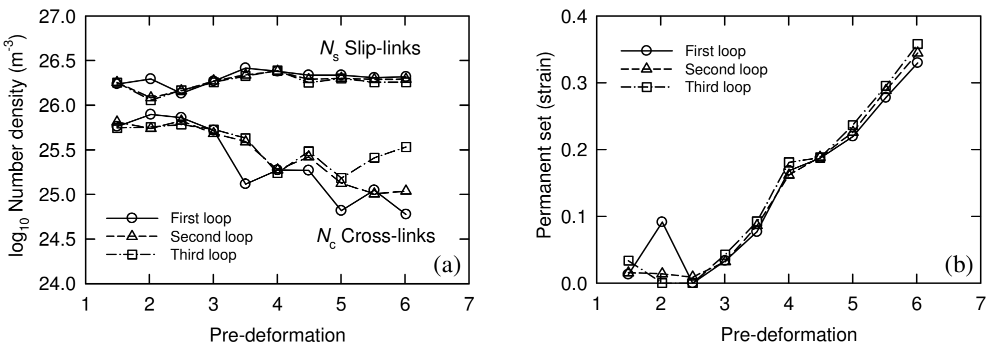

Figure 2 (a) The evolution of the number density of slip-links and cross-links with pre-deformation; (b) the strain at permanent set with pre-deformation.

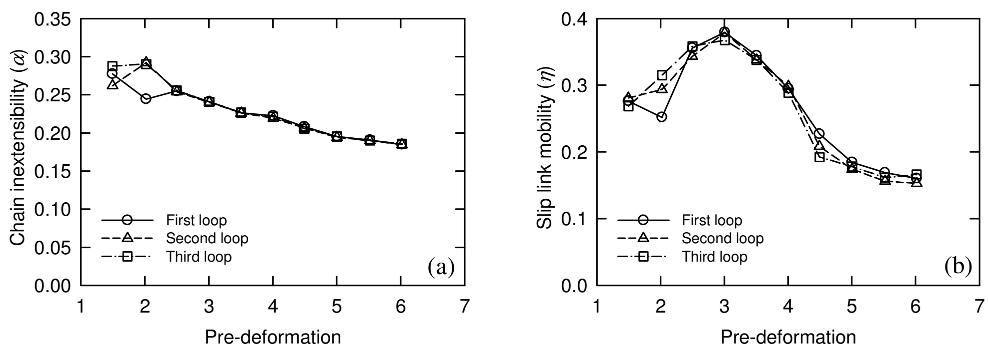

Figure 3 (a) The evolution of the chain inextensibility parameter a with pre-deformation; (b) the evolution of the slip-link mobility parameter with pre-deformation.

As can be seen from Figure 2(a), although the slip-link density as fitted to the model remains approximately constant with pre-deformation, the cross-link density appears to decrease. At the same time, Figure 3(a) shows that the chain inextensibility parameter α is also decreasing. α is related to the limiting value of the stretch λ_{max} in the EV model through $\alpha = 1/\lambda_{max}$. A possible physical interpretation of these observations 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 λ_{max}. However, the entanglements (represented by slip-links) are a topological feature of the network and therefore their number density is unaffected by strain.

Figure 3(b) shows the evolution of the slip-link mobility η. The mobility first increases, then decreases with increasing pre-deformation. At present no explanation is offered for this effect.

The entropy-elastic part of the stress, evaluated from the fitted parameters, is shown in Figure 4(a) as a function of the effective stretch seen by the rubber for all 10 tests. The data shown here were supplemented with biaxial data (not shown here) to relate the evolution of parameters to invariants of the pre-deformation.

The viscoelastic contribution to the stress was also obtained from all the loops as described above. Figure 4(b) shows the computed viscosity (away from transients) as a function of the effective stretch seen by the rubber, for all 10 tests to different degrees of pre-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. A possible explanation for this observation is that the viscous contribution arises from inter-molecular interactions that are unaffected by breakdown in polymer-filler bonding, but where the flow units are intrinsically anisotropic. With increasing strain, such flow units become increasingly anisotropic as a result of molecular alignment, and the model proposed previously presents a possible means to capture this phenomenon [4].

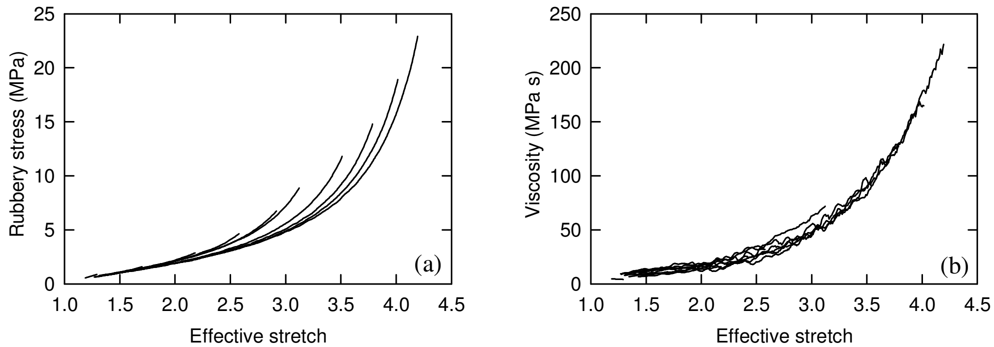

Figure 4 (a) The rubbery contributions to the stress as functions of the effective stretch for different pre-deformation levels (first loop); (b) the viscosity, calculated as viscous stress / strain rate, as a function of the effective stretch, for different pre-deformation levels (first loop).

Conclusions

This study has presented cyclic tensile stress-strain curves for a cross-linked carbon-black filled (50 phr) EPDM rubber. A technique has been proposed for extracting the network and viscous contributions to the stress and their dependence on the extent of pre-deformation. The rubbery contribution from each loop was fitted to the Edwards-Vilgis slip-link strain energy function, and the evolution of the parameters determined. This revealed that the apparent crosslink density reduced with increasing pre-deformation, but the slip-link density was constant. The viscous contribution was also invariant with respect to pre-deformation, but increased with stretch, possibly revealing increasing anisotropy of flow.

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