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Material behaviour

The role of deformation history on stress relaxation and stress memory of filled rubber

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ABSTRACT

Although the magnitudes of inelastic and viscoelastic effects in filled rubbers are small relative to that of the elastic response, these effects are nevertheless critical in applications such as gaskets, seals and dampers. This study investigates the role of deformation history on relaxation of rubber through time-dependent experiments following a range of deformation histories. Two grades of carbon-black filled EPDM were subjected to uniaxial tensile deformation followed by stress-relaxation or stress memory at fixed deformation. Stress relaxation was found to be highly dependent on strain levels following a single loading. When an additional load-unload cycle was added to the history, the rubbers relaxed an approximately constant fraction of stress after a given time, provided that the strain at stress relaxation was smaller than the historical maximum. This fraction was independent of both the applied strain and of the maximum strain, and suggests that the relaxation process is independent of scragging procedures used to control the modulus. Stress memory observed following load-unload cycles was also approximately independent of strain history.

1. Introduction

Elastomers are best known for their ability to undergo large elastic deformations, but there are many applications for which performance is dictated by the magnitude of inelastic and viscoelastic effects. For example, EPDM rubber is frequently employed in the production of seals and gaskets, and their performance is regularly evaluated in terms of compression set, defined as the degree to which a rubber remains permanently deformed when unloaded following an extended period of loading [1,2]. This reduced recovery can lead to failure in seals, and to reduced dissipation and functionality in dampers. Rubbers are inherently viscoelastic materials, however, and it can be inappropriate to talk about permanent deformation without knowledge of the response over longer timescales than those for which the material is observed. In fact, what is critical in both sealing and damping applications is precisely the time-dependence of the elastic recovery, although the timescales of interest may differ dramatically across different applications.

It is widely recognised that both the constitutive response and the viscoelastic behaviour of a rubber product are influenced by aspects such as choice of formulation, curing time and curing agents, and filler type and shape [3,4]. For example, it is well known that an increased filler fraction leads to both a stiffer response and to a greater degree of hysteresis in rubbers [4,5]. Deformation history plays an important role in the mechanical response of elastomers, best known through the manifestation of the softening phenomenon studied by Mullins and co-workers in the 1950s, and known as the Mullins effect [6,7]. In the Mullins effect, deformation causes (semi) permanent

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changes in the elastomer's microstructure that influence the mechanical response of the elastomer during subsequent deformations. As a consequence, a smaller stress is required to generate a given deformation in subsequent loadings, as long as the original deformation is not exceeded. If the deformation exceeds the historical maximum, the stress needed to deform the material becomes independent of this history, and returns to a value close to that needed to deform a virgin specimen to the same strain [4,8].

In product applications whose performance is a strong function of the inelastic response, it is an important consideration to ask whether and how the degree of inelasticity is affected by deformation history. Rubber products are regularly scragged prior to being brought into service, by subjecting them to a deformation typically greater than that expected in service [9–11]. This process is normally intended to regulate the stiffness of rubber products. By the same process, some rubber products may need to be replaced if overloaded in such a way as to move the stiffness outside acceptable bounds. However, it is not obvious whether and how the viscoelastic nature of the material is affected by scragging, and if overloads might require the rubber part to be replaced due to changes, not to stiffness, but to viscoelastic properties. The answer to this question lies in the relationship between the viscoelastic response and the deformation history.

Relatively few studies have focused on the viscoelastic response of rubber. Siouris and coworkers developed a method to record stress relaxation in elastomeric o-rings for gas turbines, focusing on the effects of lubricants and temperature [12], but did not explore the role of deformation history. Farzaneh et al. reported stress relaxation and recovery in polyurethane elastomers, focusing on the role of temperature in shape-memory applications [13]. Several studies employed an interrupted loading technique to attempt to reach an equilibrium elastic response of rubber, e.g. see [14,15] but, in general, the response during relaxation in not the focus of such experiments.

A previous study carried out by De Focatiis et al. focused on cyclic uniaxial and biaxial deformation of EPDM rubber, suggested a means by which the viscous contribution to the response could be extracted from the loading and unloading parts of a cycle [16]. Once permanent set had been accounted for, the viscous contribution during constant rate deformation appeared relatively insensitive to both the strain level during the deformation and the maximum strain reached. This was in stark contrast to the elastic contribution, which varied markedly with both current and maximum strain, in accordance with the Mullins effect. The question as to whether and how the time-dependent response during stress-relaxation and recovery might also depend on deformation history appears, to the authors' knowledge, to have remained unanswered to date. With this in mind, the present paper reports experimental measurements of short term stress-relaxation and recovery on rubber subjected to a wide array of prior deformation histories, in part inspired by the ingenious set of stress-memory experiments on polymer glasses of Caruthers and co-workers [17], 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.

2. Materials and methods

2.1. Material preparation

Two grades of ethylene-propylene-diene rubber were studied in this work. The first is a sulphur cross-linked oil extended carbon black filled (nominally 50phr) EPDM, denoted EPDM1, and kindly provided by Dr T. Alshuth from the DIK. Sheets of ~0.5mm in thickness were cross-linked by compression moulding into 150 mm × 150 mm flash moulds using a Daniels heated press at 160°C for 13 minutes [18]. The second is a carbon black filled EPDM provided pre-vulcanised in large ~0.5mm thick sheets by J-Flex Rubber Products, and denoted as EPDM2.

2.2. Physical characterisation

The densities of both materials after the vulcanisation process were measured using a Mettler Toledo XS105 analytical balance fitted with density kit, using deionised water as the medium, and rectangular specimens of mass ~0.23 g. The averages of nine repeats (±1SD) are reported in Table 1. Thermal analysis was carried out using a TA Instrument DSC Q10 differential scanning calorimeter (DSC). Cured samples of ~8 mg were first heated to 140°C at a rate of 20°C min^{-1} to erase any thermal history, then cooled to −75°C and reheated to 300°C at the same temperature rate, all in a N_2 atmosphere. The glass transition temperatures, T_g, were determined using TA Universal Analysis software as the mid-point of the temperature inflection using three tangent lines, and the averages of three repeats (±1SD) are reported in Table 1.

On the basis of equilibrium swelling experiments, an average molar mass of chains between cross-links, M_c was determined for both materials. Specimens of dimensions ~20 mm × 20 mm × 0.5 mm were immersed in analytical reagent grade toluene (from Fisher Scientific supplier) for 48 hours at room temperature (20 ± 1°C). The change in mass due to swelling was recorded with a Mettler Toledo XS105 analytical balance and used to obtain the volumetric fraction of rubber. Assuming tetrafunctional cross-links and using the Flory-Rehner equation [19], the average molar

Table 1
Physical properties of EPDM1 and EPDM2.

Material	ρ (g cm^{-3})	T_g (°C)	M_c (Da)	ρ_x (mol $m^{-3} \times 10^{-4}$)	H (Shore A)	ϕ_c^{TGA} (phr)
EPDM1	1.03 ± 0.01	−52.0 ± 1.5	1098 ± 49	4.56 ± 0.19	50 ± 1	35.5 ± 0.4
EPDM2	1.14 ± 0.01	−47.4 ± 1.0	1965 ± 11	2.54 ± 0.01	60 ± 1	64.3 ± 0.3