Polymer Testing 32 (2013) 748–759

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Property modelling

Mullins effect in swollen rubber: Experimental investigation and constitutive modelling

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ARTICLE INFO

Article history:
Received 1 February 2013
Accepted 11 March 2013

Keywords:
Mullins effect
Rubber
Swelling
Constitutive modelling

ABSTRACT

Apart from the well-known hyperelastic and large stress-strain behavior in dry rubber, the inelastic responses such as hysteresis and Mullins effect are also observed when a dry rubber is cyclically loaded. The former is given by different loading and unloading paths in a cycle, while the latter corresponds to the significant decrease in stress between two successive cycles, particularly between the first and second loading. The Mullins effect or the stress-softening effect disappears after several cycles of loading, i.e. five cycles for the materials used in the present study. A number of models describing the Mullins effect in dry rubber are available in the literature. Nevertheless, works focusing on the Mullins effect in swollen rubbers are less common. Therefore, the experimental investigation and modelling of Mullins effect in swollen rubbers are addressed in the present study. For this purpose, mechanical tests were conducted in order to probe the Mullins effect in swollen rubbers under cyclic loading conditions. Furthermore, the pseudo-elastic model [Ogden, R.W. & Roxburgh, D. G., 1999. A pseudo-elastic model for the Mullins effect in filled rubber. Proc. Roy. Soc. A. 455, 2861-2877] is considered and extended in order to account for swelling level. Results show that the proposed model is qualitatively in good agreement with experimental observations.

1. Introduction

The world is facing an energy crisis and our environment is degrading due to excessive exploration and usage of fossil fuel. Hence, several proposals have been raised to overcome this circumstance. One of the feasible solutions is through the introduction of renewable energy, e.g. biodiesel. Biodiesel, which is derived from renewable resources such as animal fat and vegetable oil, is claimed to provide better energy efficiency and offer cleaner environment. However, utilizing such fuel in the existing engine systems creates several compatibility issues for the automotive components, particularly the rubber materials [1,2]. Rubber materials are known to experience swelling when in contact with the fuel and this will contribute to deterioration of their mechanical properties. In addition to the swelling, rubber components such as o-rings or gaskets in sealing systems are also subjected to mechanical loading during their service. Therefore, it is crucial to understand the mechanical response of the swollen rubber in order to develop durable and robust components and to predict their service life [3,4].

Under static loading condition, it is well-known that rubber materials exhibit a highly non-linear stress-strain response. This response is time-dependent which can be demonstrated by relaxation and creep experiments. The hyperelasticity of the rubber material has been described using different strain energy functions and a large number of them are incorporated into commercial FEA codes. Note that the efficiency of these hyperelastic models is compared by Marckmann and Verron [5] in their review paper. In addition to the above response, when a dry rubber is subjected to cyclic loading, it exhibits strong inelastic

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0142-9418/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymertesting.2013.03.006

responses such as hysteresis and stress-softening. The hysteresis is characterized by different loading and unloading paths and can be related to either viscoelasticity [6], viscoplasticity [7] or strain-induced crystallization [8]. The stress-softening corresponds to a significant decrease in stress between two successive cycles, particularly between the first and second loadings. This phenomenon was first observed by Bouasse and Carrière [9] and intensively studied by Mullins [10]. It is often referred to as the Mullins effect. While the Mullins effect is well-known in both filled and unfilled crystallizing dry rubbers [11], it is recently demonstrated that it is also observed in swollen rubbers [12,13]. As reviewed by Diani et al. [11], there are many efforts proposing different theories to explain the stress-softening phenomenon in dry rubber. Nevertheless, to date there is no unanimous microlevel explanation for the stress-softening [11,14].

In contrast to dry rubbers, only a few studies dealing with observation of the Mullins effect in swollen rubbers and gels are available [12,13,15,16]. Moreover, corresponding constitutive models are not available in the literature. Hence, the objective of the present paper is to propose a simple phenomenological model to capture the Mullins effect observed in swollen rubbers under cyclic loading conditions. Other inelastic responses such as hysteresis and permanent set are not considered. The pseudo-elastic model of Ogden and Roxburgh [17] for the Mullins effect is modified and extended in order to account for the swelling level. The dependence of the Mullins effect on swelling is probed through mechanical testing of swollen rubbers. Two types of filled rubber are considered: Nitrile Butadiene Rubber (NBR) and Polychloroprene Rubber (CR). The experimental program is detailed in Section 2. The basic theory of pseudo-elastic model is briefly recalled in Section 3 and extended by considering the experimental observations. The efficiency of the model is assessed in Section 4. Finally, concluding remarks are given in Section 5.

2. Experimental program

2.1. Materials

Commercial grade NBR and CR materials with 60 ± 5 Shore hardness A were purchased from MAKA Engineering Sdn. Bhd., Malaysia. The NBR and CR have specific gravity of 1.4 ± 0.1 and 25 wt.% of carbon black. The vulcanization of these two materials was performed by compression molding at 165 °C for 5 min under a pressure of approximately 6.89 MPa in an electrically heated press. Due to confidentiality constraint, the detailed compound ingredients are not provided here.

The palm biodiesel (B100) used as immersion medium in this research was provided by Am Biofuels Sdn. Bhd., Malaysia. The analysis report of the palm biodiesel used in the present study is available elsewhere [18]. To systematically characterize the effect of palm biodiesel on the mechanical responses of the selected elastomers, a standard Malaysian on-road diesel fuel (B0) was also used in this study.

The rubber specimens for swelling and mechanical tests were annular cylindrical blocks with outside diameter = 50 mm, inner diameter = 38 mm and height = 10 mm.

2.2. Swelling measurement

The swelling of NBR and CR in diesel (B0) and biodiesel (B100) were measured from free swelling tests conducted at room temperature for various immersion times: 2, 5, 10, 20 and 30 days. Fig. 1 showed the simple immersion test where the specimens were hung and immersed in the stainless steel container containing biodiesel. A separate container containing diesel was used to compare the effect of different fuels on the swelling behavior of the rubbers. Each specimen was completely immersed in the tested fuel. After the desired immersion time, specimens were removed from the container and dipped quickly into acetone to remove the excess oil. The samples were then blotted dry with filter paper. The weight in air and in water for the specimen before and after immersion was measured using a balance. Note that for each immersion time, the average results were calculated from four test specimens. The volume change, ε_s was then calculated from the following relation [2]:

$$\varepsilon_s = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)}. \quad (1)$$

where M_1 and M_2 are the mass in air (gram) before and after immersion while M_3 and M_4 are mass in water (gram) before and after immersion, respectively. The degree of swelling J_s was calculated from the volume change using the following relation [19]:

$$J_s = \frac{V}{V_o} = 1 + \varepsilon_s. \quad (2)$$

where V and V_o are, respectively, the weight of swollen and dry rubbers.

2.2.1. Swelling results

The variation of degree of swelling of NBR and CR as a function of immersion time is shown in Fig. 2. The swelling in NBR and CR increases when the exposure time is increased from 2 days to 30 days. It is observed that for a given immersion time, the swelling of NBR and CR are higher in palm biodiesel than in diesel. The rate of swelling appears to be high at short exposure time before decreasing at longer exposure time. Rapid swelling is initiated with absorption of liquids when the liquids dissolve in the surface layer of the rubber (adsorption) until a certain concentration. Subsequently, the liquids penetrate slowly into the rubber by diffusion until the rubber specimen achieves equilibrium swelling [20]. Further discussion on the swelling of rubbers in palm biodiesel and diesel can be found, for example, in [1,13].

2.3. Mechanical testing for Mullins effect measurement

In order to probe the effect of swelling on the Mullins effect, uniaxial cyclic compressive tests were carried out on dry and swollen rubber specimens using an Instron test machine operated at room temperature. Circular compression plates were attached to the machine to ensure uniform displacement control on the specimens. The experimental setup was connected to a computer to record the experimental data. The tests were conducted at a constant displacement rate of 0.1 mm/s to avoid excessive increase in