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Modeling the Mullins effect in elastomers swollen by palm biodiesel

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ABSTRACT

In the present paper, experimental investigation and continuum mechanical modeling of Mullins effect in swollen elastomers, due to exposure to palm biodiesel, under cyclic loading conditions are addressed. To this end, the nature of Mullins effect in both dry and swollen elastomers is explored and compared. It is found that swelling reduces Mullins effect. Based on experimental observations, in order to account for swelling in the modeling of Mullins effect, two constitutive equations widely used in literature are considered and phenomenologically extended: Continuum Damage Mechanics model and Pseudo-Elastic model. The efficiency of the two extended models are assessed and perspectives for further development are drawn.

1. Introduction

Elastomers have distinguished themselves among polymeric materials with their own particular characteristics. They have become an almost irreplaceable important part in wide industrial applications in particular automotive components. These applications include vibration isolators, sealing system, flexible piping, gaskets and impact bumpers. During the service, these components are frequently subjected to fluctuating mechanical loading which could lead to fatigue failure (Mars & Fatemi, 2002; Andriyana, Saintier, & Verron, 2010b).

Under cyclic loading, rubber materials exhibit strong inelastic responses such as hysteresis, permanent set and stress-softening. The hysteresis may be attributed to viscoleasticity (Bergström & Boyce, 1998), viscoplasticity (Lion, 1997) or to strain-induced crystallization (Trabelsi, Albouy, & Rault, 2003). The stress-softening corresponds to a change of the mechanical properties after the material has been subjected to a deformation. More precisely, it manifests as a non-neglectable loss of stiffness during the transition from the first cycle to the second one. This softening greatly attracts the attention of many researchers after it was reported for the very first time in rubber vulcanizates by Bouasse and Carriére (1903). However, the corresponding stress-softening is often referred to as the Mullins effect after Mullins (1948). The most evident sign that stress-softening has taken place can be concluded from the stress–strain response where one can observe that a lower stress is needed to bear the same strain generated from the first loading phase. While stress-softening is

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commonly observed in filled rubbers and unfilled crystallized rubbers, no study has reported its occurrence in an unfilled uncrystallized rubber (Diani, Fayolle, & Gilormini, 2009).

As reviewed by Diani et al. (2009), there are many efforts in proposing different theories to explain the Mullins effect in dry rubber. Nevertheless, no unanimous microscopic explanation for this softening is available up to this date (Marckmann et al., 2002; Diani et al., 2009). The first attempt to describe the Mullins effect is through a phenomenological approach. Mullins and Tobin (1957) proposed that rubber initially contains both hard and soft phases. During deformation process, the hard phase transforms into the soft one. Their theory was successfully adopted in a number of works (Wineman & Huntley, 1994; Huntley, Wineman, & Rajagopal, 1996; Huntley, Wineman, & Rajagopal, 1997; Beatty & Krishnaswamy, 2000; Qi & Boyce, 2004). Simo (1987) adopted the concept of Continuum Damage Mechanics (CDM) where Mullins effect was considered as a damage phenomenon and was described by a scalar damage parameter. Thus, the material response is characterized by multiplying the classical hyperelastic strain energy with a reducing parameter representing damage level. Different forms of damage parameter were proposed in the literature (Miehe, 1995; Ogden & Roxburgh, 1999; Miehe & Keck, 2000; Chagnon, Verron, Gornet, Marckmann, & Charrier, 2004). In contrast to Miehe (1995) and Chagnon et al. (2004) who assumed that damage evolves when the applied level of deformation is undergone by the material for the first time, Ogden and Roxburgh (1999) proposed that damage stays zero when the material is subjected to a level of deformation never applied, and evolves in the range of submaximal deformation. The latter is known as the Pseudo-Elastic (PE) model.

The second approach is through physical interpretation (Govindjee & Simo, 1991; Killian, Strauss, & Hamm, 1994; Klüppel & Schramm, 9:742–754; Marckmann et al., 2002; Freund, Lorenz, Juhre, Ihlemann, & Klüppel, 2011). Marckmann et al. (2002) reported the development of a new network alteration theory to describe the Mullins effect where they considered the Mullins effect as consequence of breakage of links inside the material, involving both filler-matrix and chain interaction links. This new alteration theory was implemented by modifying the eight-chains constitutive equation of Arruda and Boyce (1993). The accuracy of the resulting constitutive equation was demonstrated on cyclic uniaxial experiments for both natural rubbers and synthetic elastomers. Chagnon, Verron, Marckmann, and Gornet (2006) later modified this network alteration theory to include the dangling chains effect in the network and proposed that the number of monomers involved in the elastic response of the material is a decreasing function of the maximum deformation. Further refinements to account for deformation-induced anisotropy in Mullins effect were proposed in the literature. Indeed, as pointed out early by Mullins (1948) and more recently by Laraba-Abbes, Ienny, and Piques (2003), Diani, Brieu, and Gilormini (2006), Itskov, Haberstroh, Ehret, and Vohringer (2006), Itskov, Ehret, Kazakevičiūtė-Makovska, and Weinhold (2010) and Machado, Chagnon, and Favier (2012), the material undergoes significant anisotropic softening due to the application of mechanical loading.

In addition to fluctuating mechanical loading, many industrial rubber components are exposed to aggressive solvents, e.g. in o-rings, hoses and sealing applications (Selvadurai & Yu, 2006). The exposure to such hostile environment is crucial since it speeds up material degradation in the form of swelling (Flory, 1953; Treloar, 1975). The corresponding degradation in rubber components is a major concern in Malaysia and Indonesia who actively develop palm biodiesel as partial substitution to conventional petroleum fuels (Jayed et al., 2011). Indeed, while the use of palm biodiesel offers an attractive alternative for diesel engines since their use does not require extensive engine modification and is environmentally friendly, it is established that utilizing palm biodiesel in the existing engine system creates several compatibility issues on the automotive rubber components (Haseeb, Jun, Fazal, & Masjuki, 2011). Thus, the need to characterize and to model the mechanical response of rubber materials under fluctuating mechanical loading taking into consideration swelling due to material exposure to aggressive solvents such as palm biodiesel becomes a critical issue for durability analysis of such engineering components.

In contrast to dry rubbers, only few studies on the observation and modeling of Mullins effect in swollen rubbers or gels are available in the literature (Webber, Creton, Brown, & Gong, 2007; Lin, Fan, Marcellan, Hourdet, & Creton, 2010; Andriyana, Chai, Verron, & Johan, 2012; Chai, Andriyana, Verron, & Johan, 2013a; Chai, Andriyana, Verron, & Johan, 2013b). Hence, the objective of the present work is to characterize and to model the Mullins effect in rubber under cyclic loading taking into consideration the swelling. For this purpose, mechanical tests are conducted in order to compare the nature of Mullins effect in dry and swollen rubbers. Moreover, two classical models for Mullins effect in dry rubber widely used in the literature are considered and extended to account for swelling: CDM and PE models. It is to note that the approach used for the development of the model in the present work is different with the one proposed by Chai et al. (2013b). Indeed, our approach is based on the split of the deformation gradient tensor into mechanical and swelling parts. The performance of the two extended CDM and PE models are discussed by comparing their ability to capture Mullins effect in swollen rubbers under cyclic loading.

2. Experimental program

2.1. Materials

The material investigated is a commercial grade of carbon black-filled nitrile rubber (NBR) with 60 shore hardness and 25 wt% of carbon-black. Due to confidentiality constraint, the detailed compound ingredients are not provided here. The specimens used in this study are in the form of hollow diabolo having a height, outer diameter, and wall thickness of 55 mm, 25 mm, and 6 mm respectively. The swollen rubber specimens are obtained by immersing dry specimens in palm biodiesel until desired swelling levels are achieved. Three swelling levels are considered: 0%, 5% and 7% in the basis of volume change, which correspond respectively to no immersion (dry), 1 week and 2 weeks of immersion duration. No standard is followed regarding the choice of the specimens and immersion durations. The detailed features of the specimen and