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Interaction between diffusion of palm biodiesel and large strain in rubber: Effect on stress-softening during cyclic loading

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ABSTRACT

In addition to fluctuating multiaxial mechanical loading, many engineering rubber components are exposed to hostile environments such as oil rich environment. In this case, the mechanical response of rubbers is affected by the interaction existed between mechanical loading and diffusion of liquid into the material. The present work attempts to investigate the above interaction and the resulting mechanical response under cyclic loading conditions in nitrile butadiene rubber (NBR) and chloroprene rubber (CR). More precisely, our focus is on the well-known stress-softening (Mullins effect) phenomenon classically observed in rubbers under cyclic loading conditions.

1. Introduction

In Asian countries such as Malaysia and Indonesia, energy insecurity, increase in energy consumption, and environmental concerns are among the major driving forces for the development of biofuels as partial substitution of petroleum fuels (Jayed et al., 2011). The use of biofuels, derived from plant materials or animal fats, offers an attractive alternative for diesel engines since their use does not require extensive engine modification. If the compatibility of materials in conventional petrodiesel system is well established, the compatibility between biofuels such as palm biodiesel and engineering materials, in particular rubbers, remain to be explored (Haseeb et al., 2010).

Rubbers are widely used in various applications such as tires, shock absorbers, seals, and gaskets in automotive industry. In a large majority of cases, they are subjected to fluctuating multiaxial loading conditions which can lead to fatigue failure (Mars and Fatemi, 2002; Verron and Andriyana, 2008; Andriyana et al., 2010). In addition, many industrial rubber components are exposed to hostile environments such as acid medium, sea water, or oil rich medium. In this case, the long-term behavior of rubbers are strongly affected by the interaction between mechanical loading and diffusion of liquids. Whenever rubbers are exposed to liquids, one main form of degradation experienced by the materials is swelling which can be described in terms of mass or volume change (Flory, 1953; Treloar, 1975). During the swelling, liquids penetrate the polymer network and occupy positions among the polymer molecules. Consequently, the macromolecules are forced apart resulting in the swelling of material and to the decrease in its strength since the increase in chain separation yields to the reduction of secondary bonding (Callister, 2007). A number of free swelling tests investigating the diffusion of liquids in stress-free rubbers have been extensively studied (see Treloar, 1975; and references herein). Furthermore, several works investigating the interaction between diffusion of liquids and large deformation in elastomers are available in the literature, namely Baek and Srinivasa (2004), Hong et al. (2008), Soares (2009), Chester and Anand (2010), Duda et al. (2010), Deng and Pence (2010) among others. Nevertheless, no attempts have been made to relate the above interaction with the mechanical response under cyclic loading and the resulting long term fatigue behavior (Zuyev et al., 1964; Magryta et al., 2006; Abu-Abdeen, 2010).

It is well-known that under cyclic loading conditions, rubbers exhibit inelastic responses namely mechanical hysteresis and stress-softening (Verron, 2003). The hysteresis corresponds to the amount of energy loss during a cycle and in the case of dry rubber can be related to either viscoelasticity (Bergström and Boyce, 2000), viscoplasticity (Lion, 1997) and strain-induced crystallization (Trabelsi et al., 2003). Stress-softening is mainly observed during the first cycles. Indeed, for a given strain level in the uploading, the stress decreases with the number of cycle before stabilizes after certain cycles depending on the characteristics of material. This phenomenon, firstly observed by Bouasse and Carriére (1903) then intensively studied by Mullins (1948), is often referred to as

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the Mullins effect. Up to this date, no general agreement has been found either on the physical source or on the mechanical modeling of this softening at the microscopic or mesoscopic scales (Dorfmann and Ogden, 2004; Diani et al., 2009).

The present work can be regarded as a first step toward an integrated durability analysis of industrial rubber components exposed simultaneously to fluctuating multiaxial loading and aggressive environments, e.g. oil environment in biofuel systems, during their service. To this end, the understanding of the interaction between diffusion of liquids and large deformation in rubber and the resulting mechanical response under cyclic loading plays an important role. More precisely, our focus is laid on the influence of swelling on stress-softening in rubbers under cyclic loading.

The present paper is organized as follows. In Section 2, the experimental works conducted are discussed including materials, specimen geometry, compression device and the types of test. The experimental results are presented and discussed in Section 3 while concluding remarks are given in Section 4.

2. Experimental program

2.1. Materials

Rubber specimens used in this research are provided by MAKA Engineering Sdn. Bhd., Malaysia. The materials investigated are commercial grade of nitrile butadiene rubber (NBR) and chloroprene rubber (CR) with 60 shore hardness. Biodiesel is prepared by blending palm biodiesel (provided by Am Biofuels Sdn. Bhd., Malaysia) with diesel. The analysis report of the palm biodiesel investigated is shown in Table 1. The immersion tests conducted are immersion in B0 (100% diesel), B25 (blend of 25% of biodiesel and 75% of diesel), B75 (blend of 75% of biodiesel and 25% of diesel) and B100 (100% biodiesel). All blend percentages are given in volume basis.

Table 1
Properties of B100 palm biodiesel.

Test	Unit	Methods	Results
Ester content	% (m/m)	EN 14103	96.9
Density at 15 °C	kg/m^3	EN ISO 12185	875.9
Viscosity at 40 °C	mm^2/s	EN ISO 3104	4.667
Flash point	°C	EN ISO 3679	168
Cetane number	–	EN ISO 5165	69.7
Water content	mg/kg	EN ISO 12937	155
Acid value	mgKOH/g	EN ISO 3679	0.38
Methanol content	% (m/m)	EN 14110	<0.01
Monoglyceride content	% (m/m)	EN 14105	0.67
Diglyceride content	% (m/m)	EN 14105	0.2
Triglyceride content	% (m/m)	EN 14105	0.2
Total glycerine	% (m/m)	EN 14105	0.25

2.2. Specimen geometry and compression device

In order to investigate the interaction between diffusion and large deformation in rubbers and its resulting mechanical response under cyclic loading condition, an annular rubber specimen having height, outer diameter, and wall thickness of 10 mm, 50 mm, and 6 mm, respectively is considered. The specimens are placed in a home-made compression device as illustrated in Fig. 1. As depicted in this figure, four stainless steel plates are arranged successively and separated by three sets of spacer bar having different heights: 8 mm, 9 mm, and 9.8 mm. Four rubber specimens are placed in each level. The plates are tightened using bolts and nuts until they are uniformly in contact with the respective spacer bar. Since the height of the rubber specimen is 10 mm, the above arrangement allows the application of different engineering pre-compressive strains to the specimen: 2%, 10% and 20%. The device containing rubber specimens is subsequently immersed into different palm biodiesel blends for durations of 30 and 90 days. The details of the immersion tests is given in Table 2. In order to determine the swelling level (change of volume), the volume of the specimen is measured before

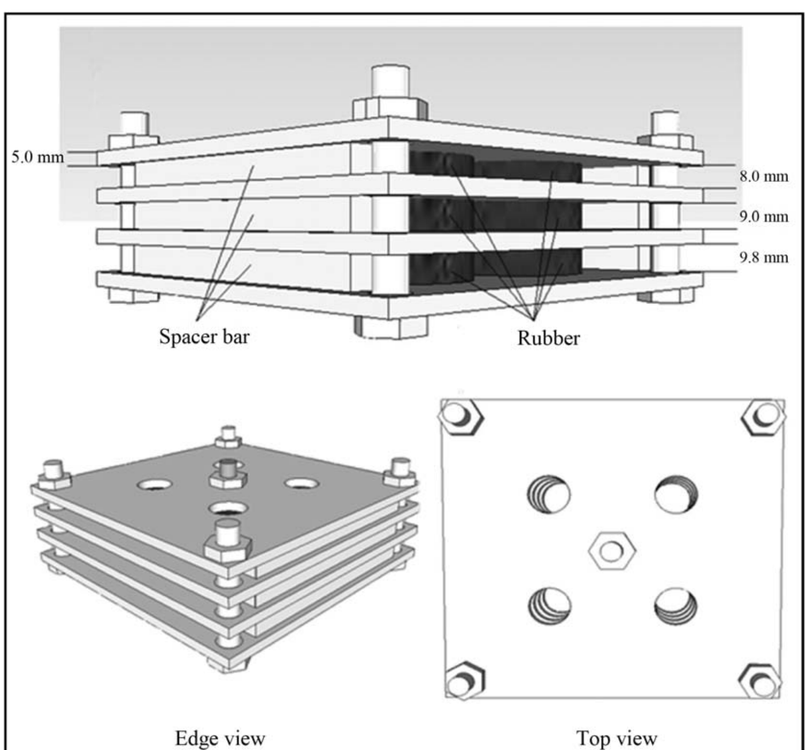

Fig. 1. Home-made compression device for the observation of the coupling between diffusion and large deformation in rubbers (Chai et al., 2011).