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Mechanical characteristics of swollen elastomers under cyclic loading

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ABSTRACT

The environmental and economic concerns have raised the popularity of biodiesel as a potential replacement for conventional fuel. However, the incompatibility of engineering rubber components with biodiesel affects significantly the performance of the components. Majority of the compatibility studies focus on evaluating the degradation of mechanical properties of the rubbers due to contamination of different types of biodiesel. Nevertheless, the resulting mechanical responses of swollen rubbers, in particularly under cyclic and fatigue loading conditions, are rarely investigated. In engineering applications where elastomeric components are concurrently subjected to fluctuating mechanical loading and contamination of hostile liquids such as biodiesel, it is crucial to investigate the mechanical responses of these components for durability analysis. In this view, the present study aims to investigate the effect of swelling, due to biodiesel diffusion in the elastomers, on the macroscopic mechanical responses under cyclic loading conditions. Simple stress-free immersion tests are conducted on elastomers and the resulting mechanical responses are evaluated. The focus of the present work is on the effect of biodiesel diffusion on the inelastic responses classically observed in elastomers under cyclic loading conditions, i.e. stress-softening, hysteresis and stress relaxation. The results show that the above inelastic responses decrease significantly when the swelling level increases.

1. Introduction

The recent oil crisis and dramatic increase in conventional fuel price have motivated the world to search for alternative fuels. One of the feasible solutions is the use of biodiesel derived from vegetable oil and animal fat. The biodiesel has been proven to be environmental friendly and provides properties similar to that of conventional fuel. However, the biodiesel has different composition from conventional diesel. Indeed, while biodiesel consists of a mixture of fatty acid ester, conventional fuel consists of a mixture of hydrocarbon [1]. This change of composition leads to difficulties in terms of material compatibility especially in industrial applications involving elastomeric materials.

The compatibility studies of several types of elastomers in diesel and palm biodiesel have been conducted [1–3]. In these works, only physical degradations related to the swelling, hardness and tensile strength of materials were studied. Trakarnpruk and Porntangjitlikit [3] evaluated compatibility of elastomers in B10 (blend of 10% of palm biodiesel and 90% of conventional diesel) after immersion of 22,670, and 1008 h at 100 °C. Six types of elastomers were investigated: NBR, Hydrogenated Nitrile Butadiene Rubber (HNBR), NBR/Polyvinyl Chloride (PVC), acrylic rubber, co-polymer Fluorocarbon (FKM), and terpolymer FKM. The authors found that the mechanical properties of NBR, NBR/PVC and acrylic rubber were affected more than those of co-polymer Fluorocarbon (FKM) and terpolymer FKM. Similar other compatibility tests of high density polyethylene (HDPE) in soybean, sunflower biofuel [4] and bioethanol [5] were conducted using different characterization techniques such as Raman and FTIR spectroscopies, and differential scanning calorimetry. Moreover, there are collections of experimental studies on mechanical responses of polymeric gels in solvents [6–8]. It is to note that the works focusing on the effect of palm biodiesel diffusion on the macroscopic mechanical responses of the rubber components, in particularly under cyclic and fatigue loading conditions are less common [9].

Under cyclic loading, dry rubber exhibits strong inelastic responses including stress-softening and hysteresis. The stress-softening corresponds to the decrease of stress level in the uploading during the first couples of loading cycles. This phenomenon, firstly observed by Bouasse and Carriére [10] then intensively studied by Mullins [11], is often referred to as the Mullins effect. Up to this date, there is no unanimous microscopic explanation for the stress-softening [12,13]. The hysteresis corresponds to the amount of energy loss during a cycle and can be related to either viscoelasticity [14], viscoplasticity [15] or strain-induced crystallization [16]. The hysteresis is found to stabilize after first couples of loading cycles.

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The present work can be regarded as a first step toward an integrated durability analysis of industrial rubber components exposed to hostile environments, e.g. oil environment in biofuel systems, during their service. More precisely, the effect of swelling, due to diffusion of palm biodiesel into rubber, on the macroscopic mechanical responses under cyclic loading condition is investigated. Two types of rubber are considered: Nitrile Butadiene Rubber (NBR) and Polychloroprene Rubber (CR).

In Section 2, the experimental procedures are detailed. The experimental results are summarized and discussed in Section 3. Concluding remarks are given in Section 4.

2. Experimental program

2.1. Materials

Commercial grade of NBR and CR with 60 shore hardness A ±5 used in this research were provided by MAKA Engineering Sdn. Bhd., Malaysia. The NBR and CR have specific gravity of 1.4 ± 0.1 and 25 wt.% of carbon black. Due to confidentiality constraint, the detailed compound ingredients are not provided here. For each type of rubber compounds, the vulcanization process was performed by compression molding process at 165 °C for 5 min under a pressure of approximately 6.89 MPa from an electrical resistance heating press. The rubber specimens for swelling and mechanical tests are annular cylindrical block with outside diameter of 50 mm, inner diameter of 38 mm and height of 10 mm. Note that no standard is followed in the determination of specimen geometry. Indeed, the wall thickness of the specimen is chosen such that swelling in the specimen during the immersion test can occur in a relatively short period of time while ensuring that specimen buckling will not occur during the compression test.

The palm biodiesel (B100) was purchased from Am Biofuels Sdn. Bhd., Malaysia. Table 1 shows the analysis report of the palm biodiesel used in the present study.

2.2. Swelling measurement

The weight of dry specimens was measured in the air and in the distilled water before the swelling test. After weight measurement, the specimens were hanged and immersed in the biodiesel bath at room temperature for various immersion durations: 2, 5, 10, 20 and 30 days. Each specimen was completely immersed in palm biodiesel as shown in Fig. 1, thereby allowing stress-free swelling to occur in the rubber specimens. When the samples reached the desired immersion duration, they were removed from the container and dipped quickly into acetone to remove the oil excess. The samples were then wiped with filter paper and the weight of swollen rubber specimens in the air and in the distilled water were measured immediately. The percentage of mass change and volume change were calculated using the following relations [3]:

$$\% \text{ Mass change} = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

$$\% \text{ Volume change} = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100 \quad (2)$$

where M_1 and M_2 are the mass in air before and after immersion respectively while M_3 and M_4 are the mass in water before and after immersion respectively. For each immersion duration, the average results were calculated from four test specimens.

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

2.3. Mechanical testing

To gain insight on the effect of swelling, due to biodiesel diffusion, on the mechanical response of elastomers, uniaxial cyclic compressive tests on dry and swollen rubber specimens were carried out using Instron testing machine operated at room temperature. Circular compression plates were attached to the machine in order 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 the temperature of the specimens, i.e. thermal effect is not considered in the present study. Two types of mechanical tests were conducted:

(1) Cyclic compressive test. The specimen was subjected to cyclic compressive loading at 40% maximum compressive strains of 6 cycles each.
(2) Multi-relaxation test. After experiencing 6 cycles of compressive loading, the specimen was subjected to relaxation tests at different strain levels during uploading and unloading.

To ensure repeatability of the results, at least three specimens were used in each test.

3. Results and discussion

3.1. Swelling

The variation of mass change and volume change of NBR and CR as a function of immersion duration is shown in Fig. 2. It can be seen that these plots show similar patterns. The swelling in both NBR and CR increases when the exposure time (immersion duration) is increased from 2 days to 30 days. The palm biodiesel uptake is relatively fast at the initial stage due to its great affinity for oil uptake [17]. The rate of swelling, either expressed in terms of mass change or volume change, appears to be high at short exposure time before decreasing at longer exposure time. Accelerated swelling is initiated with absorption of liquids when the liquids dissolve on the surface layer of the rubber (adsorption) until certain concentration. Subsequently, the liquids penetrate slowly into the rubber by diffusion until the rubber specimen achieves equilibrium swelling [18].

CR is made from emulsion polymerization of 2-chloro-1, 3-butadiene and NBR is emulsion copolymer of acrylonitrile and butadiene [19]. The polar substituent of acrylonitrile in NBR and chlorine substituent in CR contribute to their resistance to mineral oils [2]. However, the tendency of rubber to swell in solvent generally follows the principle of “like dissolve like”: polar solvent are more likely to dissolve polar substances and non-polar substances are more likely to dissolve in non-polar solvent [20]. The high polarity of ester in palm biodiesel favors the forming of