Development of an experimental device to investigate mechanical response of rubber under simultaneous diffusion and large strain compression

A.B. Chai & A. Andriyana  
Department of Mechanical Engineering, University of Malaya, Kuala Lumpur, Malaysia

E. Verron  
Institut de Recherche en Génie Civil et Mécanique, GeM UMR CNRS 6183, École Centrale de Nantes, Nantes, France

M.R. Johan & A.S.M.A. Haseeb  
Department of Mechanical Engineering, University of Malaya, Kuala Lumpur, Malaysia

ABSTRACT: Rubbers are massively used as seals and gaskets in the automotive industry where they are mainly subjected to compressive loading during their service. The introduction of biodiesel such as palm biodiesel, motivated by the environmental and economic factors, has placed additional demands on these components due to compatibility issue in the fuel system. Hence, it is crucial to investigate the durability of rubber components in this aggressive environment. A number of works on the static immersion test investigating the diffusion of liquids in rubber can be found in the literature. Nevertheless, from the experimental work viewpoint, studies focusing on the coupling between diffusion and large deformation in rubber are less common. In the present work, a compression device for coupled diffusion and large strain in rubber is developed. The apparatus comprises of four stainless steel plates and spacer bars in between which are specifically designed such that compression can be introduced on the rubber specimens while they are immersed into biodiesel simultaneously. Thereby allowing coupled diffusion and large strain to take place. Different immersion durations and pre-compressive strains are considered. At the end of each immersion period, the resulting mechanical response of rubber specimens are investigated. The features of this compression device are discussed and perspectives are drawn.

1 INTRODUCTION

Fossil fuel is depleting rapidly due to its limited reserve and increasing demands from various industry. The corresponding issue, which causes environmental degradation as well as political and economic concern, has encouraged the needs of searching for alternative fuel. One of the solution is the biodiesel which is derived from plant materials or animal fats. The biodiesel has properties similar to that of diesel and it is biodegradable and has low sulfur content. However, the fatty acid ester in biofuel is different from hydrocarbon in diesel and investigation on the material compatibility in the fuel system has been a great interest of many researchers. (Haseeb et al. 2010, Fazal et al. 2011). Indeed, in the case of rubber, changes in fuel composition often create many problems in rubber seals, pipes, gaskets and o-rings in the fuel system (Trakarnprik & Porntangjitlikit 2008).

In diesel engine, the rubber sealing components are in contact with the fuel which may lead to degradation of rubber due to compatibility issue. One main form of degradation in rubber exposed to liquid is swelling which can be described in terms of mass or volume change (Haseeb et al. 2010, Trakarnprik and Porntangjitlikit 2008). In addition to exposure to potentially hostile environments, the rubber sealing components are simultaneously subjected to fluctuating mechanical loading during their service. The durability of rubber components hence becomes a critical issue. A number of static immersion tests investigating the diffusion of liquid in rubber have been extensively studied (see (Treliar 1975) and references herein). However, investigations on more complex problems involving the swelling of polymer network in the presence of a stress (strain), in particularly multiaxial stress state, are less common. The earliest work deal with the problem dated back to the work of Flory & Rehner (1944). Since this pioneering work, more recent accounts on coupling diffusion-deformation can be found in the literature (Soares 2009, Hong et al. 2008, Baek 2004, Nah et al. 2010). It is to note that the aforementioned studies deal with the interaction between diffusion of liquid and large deformation without explicitly relating them to cyclic and fatigue behaviors of rubber.

The present work can be regarded as a first step toward an integrated durability analysis of industrial rubber components exposed to aggressive environments, e.g. oil environment in biofuel systems, during
Table 1. Properties of B100 palm biodiesel.

<table>
<thead>
<tr>
<th>Test</th>
<th>Unit</th>
<th>Methods</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>% (m/m)</td>
<td>EN 14103</td>
<td>96.9</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>kg/m²</td>
<td>EN ISO 12185</td>
<td>875.9</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>mm²/s</td>
<td>EN ISO 3104</td>
<td>4.667</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>EN ISO 3679</td>
<td>168</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>EN ISO 5165</td>
<td>69.7</td>
</tr>
<tr>
<td>Water content</td>
<td>mg/kg</td>
<td>EN ISO 12937</td>
<td>155</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH/g</td>
<td>EN ISO 3679</td>
<td>0.38</td>
</tr>
<tr>
<td>Methanol content</td>
<td>% (m/m)</td>
<td>EN 14110</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>% (m/m)</td>
<td>EN 14105</td>
<td>0.67</td>
</tr>
<tr>
<td>content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diglyceride content</td>
<td>% (m/m)</td>
<td>EN 14105</td>
<td>0.2</td>
</tr>
<tr>
<td>Triglyceride content</td>
<td>% (m/m)</td>
<td>EN 14105</td>
<td>0.2</td>
</tr>
<tr>
<td>Total glycerine</td>
<td>% (m/m)</td>
<td>EN 14105</td>
<td>0.25</td>
</tr>
</tbody>
</table>

their service. In this work, a compression device is developed to investigate the interaction between diffusion of liquids and large deformation in rubber and the effect of swelling on the mechanical response under cyclic loading in common rubbers used in sealing application such as Nitrile Butadiene Rubber (NBR) and Polyurethane Rubber (CR) is investigated.

This paper is organized as follows. In Section 2, experimental works including materials, specimen geometry, development of a compression device and the types of test conducted in this study are detailed. The experimental results are presented and discussed in Section 3. 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 material investigated is commercial grade of NBR and 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).

2.2 Specimen geometry
In order to investigate the interaction between diffusion and large deformation in rubber, a specially designed hollow cylindrical rubber specimen is used. Since the specimen will be subjected to compressive loading, its wall thickness should be large enough to avoid buckling. At the same time, it should be thin enough to ensure that equilibrium diffusion (swelling) can be achieved within a reasonable period of time. For this purpose, an annular rubber specimen having height, outer diameter and wall thickness of 10 mm, 50 mm and 6 mm respectively is used in the present study.

2.3 Compression device
The hollow cylindrical specimens mentioned in the previous subsection are subsequently subjected to different pre-compressive strains by attaching it into a specially designed compression device prior to immersion as shown in Figure 1. The compression device has special features as described below:

1. It consists of four stainless steel plates for corrosion resistance as it is to be immersed into diesel and biodiesel which are deemed to be corrosive.
2. The device is able to accommodate a total of 12 specimens arranged in 3 different levels between two successive plates.
3. Each plate has 4 main holes to allow liquid to flow and diffuse into the inner surface of the rubber specimens. In this way, each rubber specimen is subjected to diffusion of liquid from both inner and outer wall surfaces, i.e. diffusion along radial direction only as illustrated in Figure 2.
4. For each level between two successive plates, a pre-compressive strain is applied to the specimens located at the corresponding level: 20% for the level 1, 10% for the level 2 and 2% for the level 3. Different pre-compressive strains are ensured by using spacers of appropriate height. Bolts and nuts located at each corner of the plates are used to tighten the device until the compression plates are uniformly in contact with the spacers. Additional ring spacers are placed around the bolt in the middle of the plates to prevent bending of the plates.
5. In practice, the 2% strain is so small that its effect on the macroscopic mechanical response is negligible. Nevertheless, this level of strain is retained to represent stress-free condition while ensuring that the diffusion occurs only along radial direction.

In order to investigate the effect of interaction between diffusion of biodiesel and large compressive strain on swelling behavior and mechanical response under cyclic loading condition, the device containing rubber specimens are subsequently immersed into different palm biodiesel blends for the duration of 30 and 90 days. The detail of the immersion tests is given in Table 2.

2.4 Swelling measurement
The swelling of rubber specimens after immersion is described in terms of mass change and volume change and the test procedure for swelling measurement is summarized as followed:

1. Before the immersion, the weight of the rubber specimen is measured in air and in distilled water. The specimen is then quickly dipped into alcohol and blotted dry with filter paper.
2. After weight measurement, the rubber specimens are placed in sequence on the compression plates. Grease is applied on the surface of the specimens that are in contact with the compression plate to avoid bulging of the specimens. Thereby ensuring the specimens to be in a simple uniaxial compressive stress state.

3. Bolts and nuts are used to tighten the compression device until the compression plates are uniformly in contact with the spacers. The device containing rubber specimens is subsequently immersed completely into different biodiesel blends for 30 days and 90 days.

4. At the end of the immersion period, the specimens are removed from the compression device and quickly dipped into acetone; it is then clean with filter paper to remove the excess oil. The specimens are left for 30 minutes to allow for recovery before any measurement is made after immersion.

5. Step 1 is repeated to measure the weight of rubber specimen after immersion.

The percentage of mass change and volume change are calculated using the following relations (Trakarnpruk & Porn tangjitikit 2008):

\[
\% \text{ Mass Change} = \frac{M_2 - M_1}{M_1} \times 100
\]  \hspace{1cm} (1)

\[
\% \text{ Volume Change} = \frac{(M_2 - M_3) - (M_1 - M_5)}{(M_1 - M_5)} \times 100
\]  \hspace{1cm} (2)

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
Figure 3. (a) Mass change and (b) volume change of NBR and CR at different compressive strains after 1M and 3M of immersion in different biodiesel blends.

water (gram) before and after immersion. The tests are conducted on four specimens under each compressive strain and for each biodiesel blend.

2.5 Mechanical response measurement

In order to gain insight on the effect of coupled diffusion-large deformation on the mechanical response under cyclic loading conditions, mechanical tests using Instron 5500 uniaxial test machine equipped with 10 kN load cell at room temperature are conducted. To ensure uniform displacement control on the specimens, circular compression plates are attached to the machine. The experimental setup is connected to a computer to record the experimental data. All tests are conducted at a strain rate of 0.01 s⁻¹ to avoid excessive increase in the temperature of the specimens, i.e. thermal effect is not considered in the present study. The specimen is subjected to cyclic compressive loading at two different maximum compressive strains: 30% and 40% of 6 cycles each. To ensure repeatability of the results, at least three specimens are used to performed each test.

Figure 4. Stress-strain curves of a) NBR and b) CR at dry states (without immersion) and after 1 month (1M) and 3 months (3M) of immersion in B100. Results correspond to pre-compressive strain of 2%. For immersed rubbers, the stress is expressed with respect to unswollen-unstrained configuration (dry cross section).

3 RESULTS AND DISCUSSION

3.1 Swelling of rubber

Figure 3 shows the percentage of mass change and volume change of NBR and CR with different compressive strains (2%, 10% and 20%) after immersion in different biodiesel blends (B0, B25, B75 and B100) for 30 days (1M) and 90 days (3M) respectively. Both plots show similar patterns. The percentage of fuel uptake is increasing with the increase of palm biodiesel content. It is clear that for low biodiesel content (B0 and B25), no significant fuel uptake is recorded for NBR. At the higher percentage of biodiesel content (B100), both NBR and CR shows significant mass change and volume change. The corresponding trend can be attributed to the segmental mobility of the polymer and free volume of the polymer (George 2001). Several factors influencing the segmental mobility of the polymer chain including unsaturation, crosslinking degree, crystallization and nature of the substituents. The nature of the substituent is particularly critical in
this study. This is because CR is made from emulsion polymerization of 2-chloro-1, 3-butadiene and NBR is emulsion copolymer of acrylonitrile and butadiene (Dick 2001). The polar substituent of acrylonitrile in NBR and chlorine substituent in CR are resistant to oil absorption. However, the swelling of rubber is by the principle of “like dissolves like” – polar solvent are more likely to dissolve polar substances and non-polar substances are more likely to dissolve in non-polar solvent (Zhang & Cloud 2007). The high polarity of ester in palm biodiesel favors the forming of polymer-solvent interaction resulting to the increase of swelling in CR as the ester content in the palm biodiesel blend increases (Pekcan 2002).

In addition, it is observed that the fuel uptake is affected by the level of compression, except for CR after 3 months immersion. The increase of pre-compressive strain has restricted the fuel uptake into the elastomeric materials, i.e. the compressive stress appears to reduce the amount of swelling compared with that for stress-free rubber. Absorption of liquid into rubber occurs when liquid dissolve on the surface (adsorption) and penetrate further into the rubber by diffusion. As the compressive strain increases, the initial effective area for diffusion to occur along radial direction in hollow cylindrical rubber specimens becomes smaller. Hence, the resulting swelling is lower. Furthermore, the reduction in swelling of rubber is affected by the hydrostatic component of the applied stress. A compressive stress, for which the hydrostatic component is positive leads to a decrease in the swelling of rubber (Treloar 1975, Fukumori et al. 1990). The fluctuating trend of CR after 3 months immersion in B100 might be caused by the maximum swelling in the polymer network and strong polymer-solvent interaction which has remedied the effect of compressive strain.

3.2 Influence of swelling on the mechanical response of the rubbers

The mechanical response of NBR and CR corresponding to 2% pre-compressive strain after immersion in B100 under cyclic compressive loading at two different maximum compressive strains are depicted in Figure 4. To compare the mechanical response of the swollen rubber with the dry rubber (unswollen), the compressive stress of the swollen specimen (after immersion) is computed by dividing the measured compressive force with the unswollen unstressed cross section. For each maximum compressive strains, the specimen experiences six cycles of loading. It is shown that there is not much difference in the nature of stress-strain behavior after immersion. However, lower stress is recorded for CR after 90 days immersion given the same pre-compressive strain. The corresponding behavior can be related to the swelling in the CR which decreases its strength due to strong interaction of rubber-solvent matrix system (George 1999).

According to Treloar’s theory (Treloar 1975), the only effect of the swelling is to reduce the modulus in inverse proportion to the cube root of the swelling ratio, without changing the form of the stress-strain relations, i.e.,

$$G' = V_2^{1/3} \frac{G}{V}$$

(3)

where $G'$ and $G$ are respective shear modulus in swollen and dry state and $V_2$ is volume fraction of rubber in the mixture of rubber and liquid. In Figure 5, three types of shear modulus ratio are plotted as a function of applied compressive strain. The first one is the cube root of the swelling ratio as predicted by Treloar in Equation 3. Secondly, the shear modulus ratio is obtained by fitting the first uploading response
of the stress-strain curve by assuming the response can be represented with Neo-Hookean model and the third ratio is obtained from the real experimental data (equivalent with the ratio of stresses at swollen and dry states) as shown in Figure 5 (a) and (b). The same shear modulus ratios are plotted in Figure 5 (c) and (d) by using the equilibrium response. In our case, the equilibrium response is given by the imaginary curve lines between the uploading and unloading of the 6th cycle, after stress-softening effect is removed (Bergström & Boyce 1998). All the plots in Figure 5 shows that the shear modulus ratio deviates from the cube root of the swelling ratio as predicted by Trelloar. This might be attributed to the fact that Trelloar assumes rubber networks to follow Gaussian statistical model.

4 CONCLUSIONS

In the present work, a simple device for the observation of the interaction between diffusion of liquids and large deformation in rubber was developed. The device consists of four stainless steel plates with spacer bars in between. The presence of spacer bars allow the introduction of pre-compressive strain while exposing simultaneously rubber specimens to biodiesel. It was found that the swelling in rubbers increases with the increase of palm biodiesel content and decreases with the increase of pre-compressive strain.

The effect of the presence of biodiesel on the mechanical response of rubber was also studied. It was observed that the presence of biodiesel and the increase in its content reduce the mechanical strength of the rubber. Furthermore, the shear modulus ratio of swollen and dry rubbers is found to deviate from the one predicted by Trelloar.

Finally, it is to note that only uniaxial stress state is observed in the present study. Further investigation on how multiaxial stress state plays role on the diffusion is needed.

REFERENCES


