Characterization of Rubber Degradation in a Brake Wheel Cylinder under Cyclic Loading

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ABSTRACT

Rubber has been widely employed in the automotive industries in various components. One component that benefits rubber is the braking system which is essentially for stopping the vehicles safely. This investigation intends to characterize the rubber degradation by applying pre-determined cyclic loadings; 10,000, 100,000, and 500,000 cycles which implicated the deformation of this rubber in the brake wheel cylinder while in service. The residual compression properties of rubbers were determined by using a uniaxial compression test. The damage development in rubbers was characterized using X-ray crystallography (XRD), pyrolysis gas chromatography-mass Spectrometry (GC-MS), and scanning electron microscope (SEM). The result indicates the rubber degradation is clearly visualized in the compression test for which lower stiffness is associated with higher cycle specimens. There is evidence of microcracks formation in SEM images which indicates the softening effect of the 100,000 cycles sample. There is a positive correlation between the number of cycles and the peak height intensity in the programs of GC-MS. In addition, the XRD results indicate evidence of crystallization reduction on the damaged samples as samples degrade under cyclic loading.

Keywords: *Brake Wheel Cylinder; Rubber; Cyclic Loading; Damage Development*

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Introduction

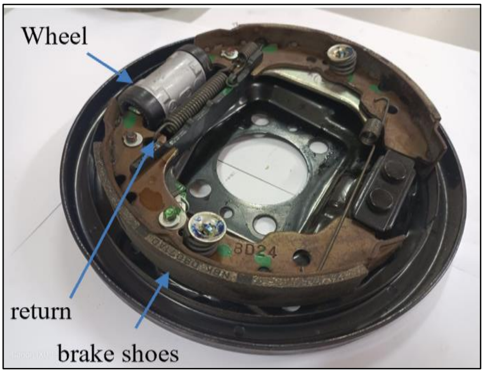
Rubbers are versatile materials with such variety of applications in industries such as construction (earthquake resistance building), airplanes, automotive, and general consumer products [1]. Rubber can be classified into two categories: natural rubber and synthetic rubber. The former is obtained from the latex sap of rubber trees while the latter is produced by synthesizing from petroleum-based products. Rubber is a polymer material, and very elastic at room temperature. From a materials engineering perspective, rubber has both hyperelasticity and viscoelasticity characteristics. The former results from the conformational entropy change of rubber macromolecular chains while the latter is caused by the internal friction of the materials [2].

In the automotive industry, some parts use rubber in the vehicle components either in critical or non-critical applications. The brake wheel cylinder, which is the main component in the drum brake, is one of the most critical components in the braking system. The main component of the drum brake is brake wheel cylinder, brake shoes and return spring as shown in Figure 1a. When a brake pedal is applied, the brake wheel cylinders work by allowing pressurized hydraulic changes into mechanical forces that push the shoes brake against the inner surface of the drum. As illustrated in Figure 1b, the brake wheel cylinders contain rubber parts: dust boots, and a cup expander which are subjected to repetitive expansion and retraction while braking.

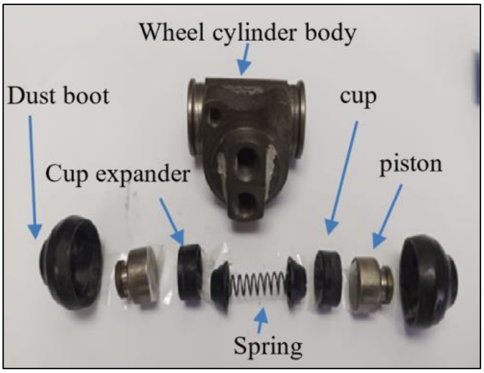
The repeated cyclic loads while braking may cause rubber in brake wheel cylinder to degrade over time. These repetitive stresses could initiate cracks and break in after a certain number of repeats, indicating this is a case of fatigue in rubber. Fatigue failure is caused by the local stress concentrations occurring around defects in the internal structure [3]. The rubber boots and seals in wheel cylinders may get fatigue damaged during operation. Foreign particles such as dust and other impurities may slip into the braking system and this could cause a leak and piston jam in the wheel cylinders [4]. As a result, these leaks and piston jams may compromise braking performance, leading to major fatal accidents. In addition, the failed wheel cylinders are barely noticeable due to the fact the wheel cylinders themselves are contained in the drum brake hub enclosure, and getting a direct visual inspection can be challenging.

The study of rubber degradation in automotive components has been reported in the literature such as car wiper rubber blade [5], rubber hoses for car radiators [6] and engine rubber mounting [7]. There are also many studies undertaken on fatigue damage on rubbers materials. Ruellan and co-workers [8] found that crystallization of natural rubber was reduced with the rising temperature in the uniaxial tensile fatigue tests. The influence of different filler on the fatigue resistance was studied by Dong et al. [8] on natural rubber. They found fatigue resistance on natural rubber was improved with carbon black filler but with carbon nanotube (CNT) filler, fatigue resistance was weakened.

Other authors such as Belkhira et al. [9] had proposed new model to predict fatigue life of rubber parts using cracking energy density (CED) method. The conclusion obtained by these scholars was indeed very good, but the information is still not sufficient. Based on careful literature research, there is no other research looking at the use of rubber for the brake drum cylinder.



(a)



(b)

Figure 1: Schematic diagram of; (a) drum brake, and (b) its internal components

The aim of the investigation is to understand the damage progressions of rubber components of brake wheel cylinders applications subjected with a pre-determined number of cycles; 10,000, 100,000, and 500,000 cycles, respectively. The onset damage development after each cyclic test was characterized using axial compression test, X-Ray Crystallography (XRD), Scanning Electron Microscope (SEM), and Pyrolysis Gas Chromatography-Mass Spectrometry (GC-MS) between the undamaged (uncycled) and damaged samples. This work may be of interest to both Malaysia's local automotive and rubber industries, inspiring more discovery and advancement of the knowledge in rubber materials.

Methodology

Samples preparation

In this investigation, the brake wheel cylinder designated for Proton Saga BLM (2008-2012) model was chosen for this study. The brake wheel cylinders were acquired from a local automatic spare part store. There was neither further physical information supplied by the manufacturer, nor the specification of rubber materials used in the brake wheel cylinder that came with the packaging box. The characterization route of rubber in this research is depicted in Figure 2. The ASTM and ISO standards requires the fatigue test configuration to follow dumbbell-shaped specimens [2] but in this investigation, the modification on the rubber geometry was deemed impossible. Therefore, a special jig was designed to mount and hold the brake wheel cylinder during the compression cyclic loading and uniaxial compression test as shown in Figure 3a. Comparison of damaged samples (cycled) was made with undamaged (uncycled) samples.

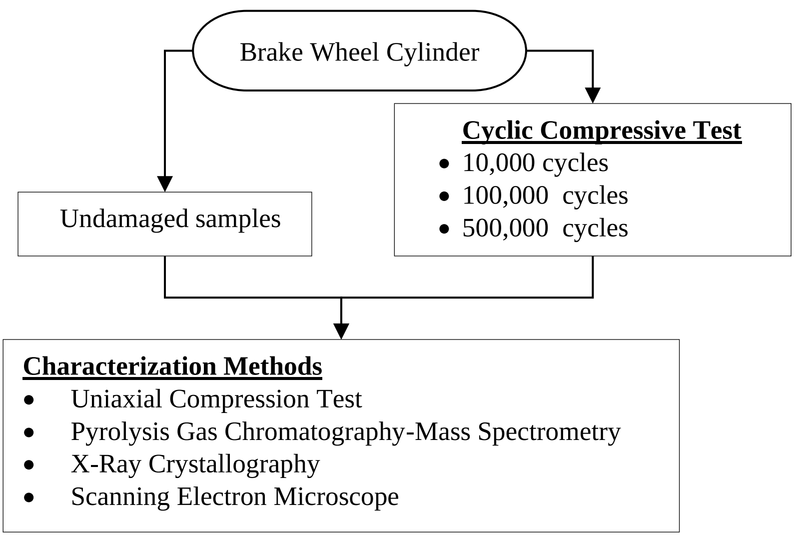
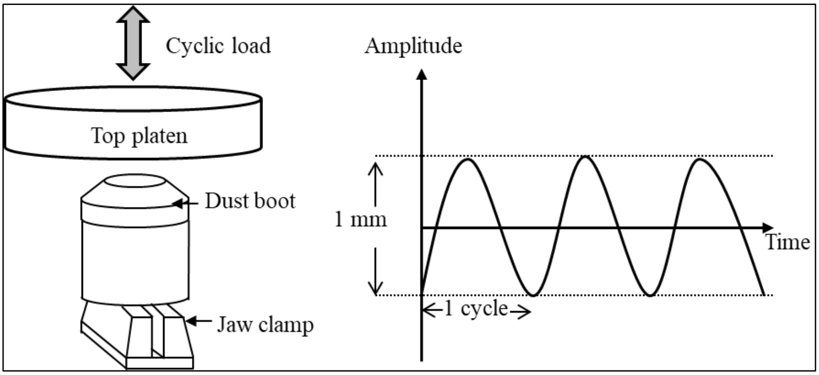


Figure 2: Process flow chart showing the applied characterization route of samples

Uniaxial compression test

<u>Cyclic compressive test</u>

To gain insight on the rubber's degradations due to expansion and contractions of brake wheel cylinder, uniaxial cyclic compressive tests was conducted using a Instron testing machines a 1 kN load cell. The tests were carried out at several cycles: 10,000, 100,000, and 500,000. The machine will automatically stop operating when the desired number of cycles had been completed. A constant amplitude-controlled loading method was followed throughout the cyclic test as described in Figure 3b. A low frequency of 5 Hz was selected throughout the duration of the test to replicate the movement of the rubber, assuming the brake wheel cylinder is operated during normal conditions. The amplitude refers to how much the rubber will be compressed during the period of cycles under cyclic loading.



(a) (b)

Figure 3: (a) Schematic of uniaxial cyclic compressive tests, and (b) constant amplitude-controlled loading method used in this study

<u>Residual compressive test</u>

The residual compression strength of rubber after pre-determined cyclic test was measured using the same Instron machine and test set-up as shown in Figure 3a. Measurement of rubber physical parameters such as inner and outer diameter, width, and height were initially taken. The samples were compressed up to the lowest predetermined height of rubber. The compressive stress, σ was calculated by simply dividing the compressive load, F with the rubber cross section area, A accordingly. The compressive strain, ε was determined by dividing the decrease in length by the initial height of the rubber. A control sample which represents the undamaged rubber had been tested to get a strength benchmark. The stiffness of the rubber, E was calculated from the linear region of the curves in the 1-2% of strain by the following equations: -

$$E = \frac{\sigma}{\varepsilon} \tag{1}$$

Scanning Electron Microscope (SEM)
The surface morphology study of rubber was done using a Gemini Scanning Electron Microscope. A small sample was cut off and placed on a metal stub with adhesive tape on it. Subsequently, it was sputter-coated before SEM imaging. The acceleration voltage was adjusted to between 2 kV and 9 kV for optimized imaging.

X-Ray Crystallography (XRD)
X-Ray Crystallography analysis of the samples was carried out using Philips Expert Pro Mr Pw3040 X-ray diffractometer in the 2θ range 20°-100° to examine the change of crystalline nature of rubber before and after compression cyclic loading.

Gas Chromatography-Mass Spectrometry (GC-MS)
A pyrolysis test was carried out at the Forensics Laboratory at the Faculty of Applied Science, UiTM Shah Alam using a Shimadzu Scientific Instruments - GCMS-QP2010 Plus model. A small amount of rubber (internal diameter 0.5 mm) was cut out from the main sample using a scalpel and it was weighted about 20 mg for GC-MS testing. The rubber was placed in the reactor and burned constantly at a temperature of 800 ºC for about 45 minutes in a nitrogen environment. The data acquisition system and parameters control were done using GCM solution software. The identification of chemical compounds was referred in the NIST 08 mass spectral library.

Results and Discussion

Compression properties
Figure 4 presents the compression stress and strain behaviour of rubber wheel cylinders after various compression cyclic loadings. The curves began with a linear trend up to 10% of compression strain which attributes to the elastic properties of the rubber materials. It is interesting to see there is a sudden increase of slopes in the curves which are seen around half of compressive strain. The curves continue to increase up to the peak of the curves which is about 0.10 MPa. The 500,000 cycles samples show the highest residual compressive deformation compared at maximum of 45% of compressive strain in comparison to the 100,000 cycles, 10,000 cycles, and undamaged samples.

A closer inspection of the curves shows there were noticeable changes in the slopes for the 100,000 cycles and 500,000 cycles, where it has lower gradients than the undamaged and 10,000 cycles. For the 100,000 cycles sample, there are slight decreases in compression stress are noticeable on the curves. Further compression stress drop can be seen on the 500,000 cycles. The behaviour may indicate that the component exhibits Mullin's effect [10], a stress-softening effect after prolonging cyclic test caused by the bond ruptures or elastomer chain slippage [11]. Mullin's effect involves the evolution of intrinsic structures such as micrometre or submicrometric cavities or known as microcracks [10].

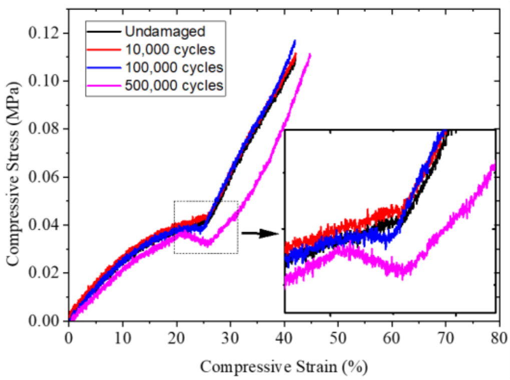


Figure 4: Typical compressive stress-strain curves of rubbers after compressive cyclic loading

The residual compression stiffness of specimens at the specific number of cyclic compressions measured at the first linear region of the curves is shown in Figure 5. The undamaged samples show a maximum value of 0.300 MPa. The rubber in brake wheel cylinder show loss in stiffness with cycling. The 10,000 cycles samples show a reduction to 0.280 MPa. The residual stiffness remains consistent at 100,000 cycles but there is a sharp decline to 0.238 MPa when the specimens were cycled at 500,000, suggesting greater damages in the samples.

The damage can be visualized in SEM micrograph where the formation and growth of multiple microcracks on the rubber surface of 100,000 cycle samples is shown in Figure 6b as compared to the undamaged samples in Figure 6a. This finding is consistent with that of Quang et al. [12] which they found cracks formation in natural rubber (NR) after cyclic loading that is associated with Mullin effects. It is believed that the alternating and long-term compression stress causes the breakage of chemical bonds, leading to the molecular break and ultimately, forming a crack. From the secondary perspective, the shear stress destroys secondary bonds, causing relative slippage of molecular chains and cracks [2].

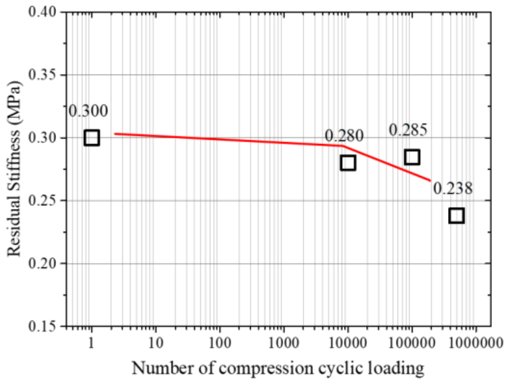


Figure 5: Residual stiffness against number of compression cyclic loading between undamaged and damaged specimens

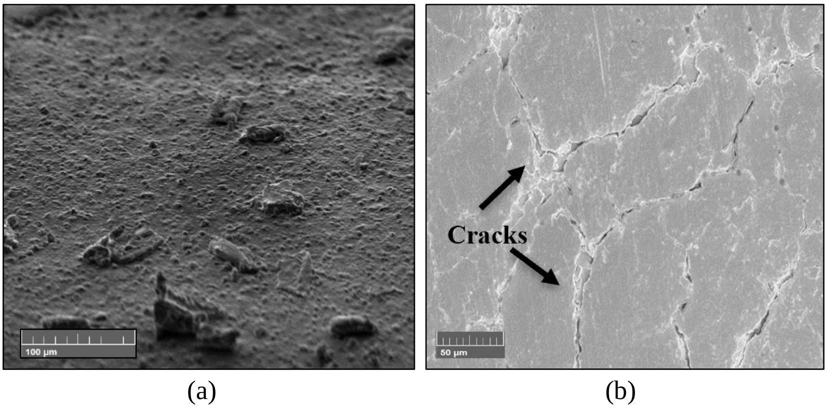


Figure 6: SEM micrograph of; (a) undamaged rubber (500 X magnification), and (b)100,000 cycles rubber (1000 X magnification)

XRD analysis

The XRD technique is performed by many researchers to illustrate the crystalline nature of rubber [13]–[15]. The diffraction peak height indicates the crystallinity regions while the broadening diffraction implies the amorphous structure of a material [16]. Therefore, the position and the intensity of X-ray crystallography peaks may indirectly present damage development of rubber after cyclic loadings. By observing the rubber's XRD in Figure 7, the difference between the undamaged rubber compared to damaged rubber is clearly observed. It is rather interesting that some major peaks in the XRD have disappeared at the ~39°, ~48°, ~64°, ~81° and ~98° spectrum, respectively.

However, it appears that there is no appreciable difference between the damage samples, 10,000, 100,000, and 500,000, respectively can be seen here. The damaged samples have significantly lower intensity as compared to undamaged samples. The combination of absence and lower peak height may suggests the crystallization of rubber declines because of repetitive cyclic loadings, possibly by the oxidation of the rubber, leading to changes in molecular into loose and unpacked structures [14]. Crystallization plays an important role in the mechanical properties of polymer for which it may prevent crack growth under substantial deformation [17]. Hence, this would explain the loss of compression stiffness and higher strain in the compression test (Figure 4).

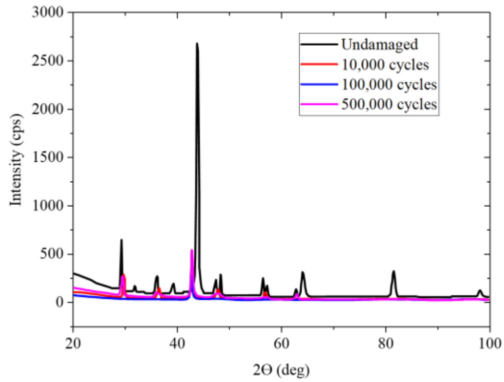


Figure 7: XRD pattern between undamaged and damaged samples under cyclic loadings

Pyrolysis GC-MS spectra analysis

Kusch et al. [18] demonstrated that the application of pyrolysis GC-MS was able to perform failure analysis in the rubber tyre for both qualitative and quantitative information. Figure 8 shows the pyrograms of the examined rubber samples pyrolyzed at 800 °C. There are many peaks available in the pyrograms across the time that made identification of the main chemical elements of the rubber not straightforward because industrial rubbers contain various additives such as plasticizers, carbon black, inorganic fillers, antioxidants, cross-linking agents, and others that essentially give particular physical and/or chemical properties [19].

With the help of the mass spectra database library NIST 08, further examination of all detected peaks suggests the identified pyrolysis rubber product as styrene-butadiene rubber (SBR) for which 2-Phenyl-1,3-butadiene monomers can be found in time = 9.8 minutes [20]. SBR is common rubber for car tyres and products for automotive. Other related pyrolysis products of SBR found in this pyrogram are toluene, benzene, pyrene, and indene [18].

The result of this study shows that pyrolysis compounds measured by peak height increase as the cyclic loading increases, suggesting some chemical compounds have been intensified.

Interestingly, the increased peak height of pyrograms corresponds to the decrease of rubber's stiffness as cyclic loading increases as shown in the compression test (Figure 4). Such increase of peak height in the pyrolysis diagram can also be noticed in the research by Yang et al. [21] where they studied the effect of before and after thermal oxidation on high-density polyethylene (HDPE) composites. Therefore, this suggests the intensified peak height of the pyrolysis product probably means is a positive indication of damage in rubber.

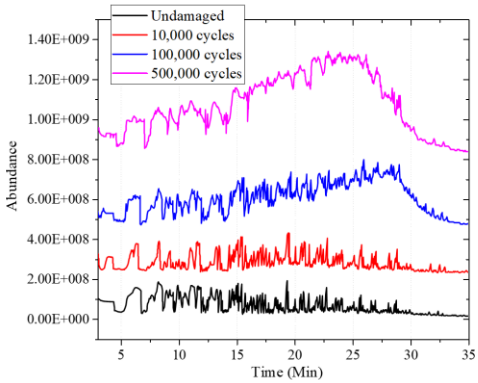


Figure 8: GC-MS comparison between undamaged and damaged rubber

Conclusions

In this investigation, the influence number of load cycles; 10,000, 10,000 and 500,000 cycles to the damage progression of rubber component in brake wheel cylinder was studied. The stress-softening effect was observed in the damaged samples in the compression test. The increasing cyclic loading of up to 500,000 cycles caused a greater stress-softening effect. The scanning electron microscopy analysis has revealed the presence of microcracks in the damaged rubber. The XRD analysis showed some major peaks disappeared between damaged and undamaged samples, showing of a decrease in crystalline region in the damaged rubbers. However, it seems there are no appreciated differences in the peak height between 10,000, 100,000, and 500,000 cycles samples. The GC-MS pyrograms could identify the type of rubber in this component, which is mainly composed of styrene-butadiene rubber. Some pyrolysis compounds were intensified as the cyclic loading increased which corresponded to the damage experienced by the rubbers.

Contributions of Authors

The authors confirm the equal contribution in each part of this work. All authors reviewed and approved the final version of this work.

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Conflict of Interests

All authors declare that they have no conflicts of interest.

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