Characterisation of static and dynamic responses of natural rubber bio-composites

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Abstract. Characterisation of static and dynamic behavioural are presented in this study of hybrid filled natural rubber. The hybrid filler consists of a combination of oil palm ash (OPA) and egg shell powder (ESP). Testing on the samples are conducted in three different aspects namely static compression testing, time dependent stress relaxation testing in compression and dynamic compression testing. Mechanical properties such as the static stiffnesses, hysteresis loss ratios, stress relaxation responses, dynamic stiffnesses, phase angles and damping ratios are reported. The static stiffness values of the hybrid filled rubber, although lower than rubber filled carbon black, presented potential if the ESP content were to be increased. The stress relaxation responses lacked consistency in the uploading stages but were fairly consistent in the unloading stages where the relaxation was close to that of rubber filled carbon black. The dynamic properties appear to be no significant improvement over that of rubber filled carbon black filled. All hybrid filled rubber samples conformed to general dynamic properties of viscoelastic material and did not display any unexpected behaviour. Collectively, there is a trend of improvement with increasing ESP content but no prominent improvement over rubber filled carbon black is observed.

1. Introduction
A majority of rubber is used in anti-vibrational and shock absorbance applications include tyres, rubber isolators and seismic bearings as their energy dissipating capacity and viscoelasticity generally outperform that of other materials [1]. Rubber’s ability to conform to any surface it comes into contact with also enables it to be an effective seal in engine gaskets, window seals and waterproof seals [2]. Natural rubber on its own has limited adaptability, hence to improve its properties, fillers are usually mixed in during production. The most common type of rubber filler used today is carbon black. Carbon black is an unsustainable option for rubber fillers as it is manufactured by the intentional incomplete combustion of petroleum products [3]. This petroleum based filler is mainly used because it has superior filler properties to almost all other types of fillers. This in itself presents two problems. Firstly, petroleum will face eventual depletion making it a non-sustainable source of rubber fillers. Secondly, carbon black filled rubber is difficult to recycle. The aftermath of this on the environment is catastrophic as the tyres are non-biodegradable. Efforts in recycling rubber tyres are possible but these are limited in terms of processing rates, cost, as well as technology [3]. Today, the main method of recycling rubber is by cryogenic crushing where the rubber is frozen using liquid
nitrogen and crushed to a powder and melted to be reused in other industries [4]. Cryogenic crushing of carbon black rubber however is very energy intensive and costly. Hence, one solution is to replace the type of fillers used in natural rubber. In this study, the filler used is a hybrid made up of both egg shell powder (ESP) and oil palm ash (OPA). The advantage of using this hybrid filler is the wide availability of the material, cost potential as well as sustainability prospects as they are made from natural sources. The main advantage of using bio-fillers is their reduced harm to the environment. Research has been conducted on the ability of OPA [6] and ESP [7] to be used as fillers individually. It can be proven that ESP has excellent toughness and strength on its own as a filler and, in addition to that, it can be observed that properties such as the stress softening and hysteresis loss are not diminished by the use of bio-fillers [8].

This paper will focus on the effect of varying the content of the ESP against static compression testing, stress relaxation testing and dynamic testing to analyse the properties of the hybrid filled rubber. As a whole, the results of this study can serve as a reference point for behavioural characteristics of OPA/ESP hybrid filled rubber under both static and dynamic compression testing.

2. Materials and Methods

2.1 Materials

Five different of rubber compounds were mixed at Rubber Research Institute of Malaysia. Each compound was mixed using two roll mill machine and cured using press machine at the temperature of 140°C in the shape of hardness button with a dimension of 8mm in thickness and 44mm in diameter. The composition of each compound is described in Table 1. Their compositions are described in table 1.

Table 1. A composition of rubber compounds.

| Rubber Compound Id. /Ingredients (phr) | Natural Rubber (NR) | OPA/ESP10 | OPA/ESP20 | OPA/ESP30 | Carbon Black |
|--------------------------------------|---------------------|-----------|-----------|-----------|-------------|
| SMR Lb                               | 100                 | 100       | 100       | 100       | 100         |
| Zinc Oxide                           | 5                   | 5         | 5         | 5         | 5           |
| Stearic Acid                         | 1                   | 1         | 1         | 1         | 1           |
| CB N550                              | -                   | -         | -         | -         | -           |
| Eggshell Powder                      | -                   | 10        | 20        | 30        | -           |
| Oil Palm Ash                         | -                   | 1         | 1         | 1         | -           |
| Permanax TMQc                        | 1                   | 1         | 1         | 1         | 1           |
| Sulphur                              | 2.5                 | 2.5       | 2.5       | 2.5       | 2.5         |
| CBSd                                 | 0.5                 | 0.5       | 0.5       | 0.5       | 0.5         |

a parts per hundred of rubber
b Standard Malaysian Rubber Grade L
c 1,2-dihydro-2,2,4-trimethyl quinolone
d N-cyclohexyl-2-benzothiazole sulphonamide

2.2 Methods

2.2.1 Static compression tests

The static compression test was carried out on an Instron 5582 Universal Testing Machine (UTM) with a 100kN capacity of load cell. Figure 1 shows the uniaxial compression set up. Emery paper of grit 120 was used to prevent the samples from sliding during the compression cycles. The machine software, Blue Hill, is used to create a compression testing procedures. Virgin samples were used to obtain a highest possible accuracy. The strain magnitudes were kept constant at 40% thickness for all samples to ensure all responses obtained were based on material properties rather than situational properties.
Before compressing, the virgin samples were measured with a vernier calliper to obtain their diameters, thicknesses and hence the depth of compression to achieve the required compression strain. All tests were carried out at a rate of 5mm/min up to 40% of the sample thickness and once reached, the compression reverses back to 0% strain. This cycle is repeated 5 times and all tests were conducted at room temperature. Although, temperature has a significant influence on the stiffness of rubberlike materials [9], all tests were conducted at room temperature to establish a more fundamental understanding on the effect of the hybrid filler first.

2.2.1.1 Maximum Compressive Stress at 40% Strain
The maximum stress is obtained by simply reading the maximum response at 40% strain. This is a simple yet good way to directly compare material properties and determine if the material being tested possesses any improved characteristics or has potential to improve upon conventional materials.

2.2.1.2 Static Stiffness
In order to calculate the static stiffness, two points are taken from the loading curves for each material on a force vs. displacement graph. Equation 1 below is then used to calculate the static stiffness of each individual material where F is the force and x is the displacement (strain) at points 1 and 2 on the loading curve.

\[
Static\ stiffness, \ K_s = \frac{F_2 - F_1}{x_2 - x_1}
\]  

2.2.1.3 Hysteresis Loss Ratio
The hysteresis loss ratio is defined using the energy provided to the rubber sample during the uploading phase and the energy loss during the unloading phase. Essentially the energy dissipated is represented by the difference in area of the uploading and unloading curves and the energy supplied is represented by the area under the uploading curve on a stress vs. strain graph [9]. The purpose of using fillers are to increase the hysteresis loss ability of rubber so that it may absorb more energy during vibrational damping or shock absorbance [10].
Figure 2 represents a generic hysteresis curve with the hysteresis loss ($W_1$) and area under the unloading curve ($W_2$). Hence, to calculate the hysteresis loss ratio equation 2 is used.

$$Hysteresis\ loss\ ratio = \frac{W_1}{W_1 + W_2}$$ (2)

2.2.1.4 Stress relaxation

The stress relaxation test was also conducted using an Instron 5582 Universal Testing Machine by creating a testing program using a Blue Hill software. The physical set up of the test is identical to that of the compression test. In the case of a stress relaxation test, all samples used were pre-stressed from the compression tests to simulate real loading and relaxation conditions. Testing conditions used were similar to the compression tests with a strain rate of 5mm/min. The static strain regions profiled into the testing parameters are 20 minutes long and occurred at every 15%, 30% and 45% strain on both loading and unloading. The dimensions of the samples used in the stress relaxation test were recorded previously and the strain levels for each sample were calculated individually based on the sample thickness. The main purpose of the final static region (45% strain) is to obtain distinct results for the region before and after completion of the test. This is because the results for the final relaxation region is often difficult to read due to the values of the static region blending in with the values of the unloading region immediately after it. Hence, since results for strain levels up to 30% are desired, an additional strain level is tested at 45% strain. Figure 3 shows the strain profile used in this test.

Figure 3. Strain profile for stress relaxation test.

The results of the stress relaxation test will indicate the stress relaxation ratios of each material. Stress relaxation is the residual elasticity present in the material up to the point where it achieves equilibrium stress. In order to compare the stress relaxation capacity of each material at each strain magnitude, they are converted into a relative form. The ratios of the relaxation stress with time at each strain level, $\sigma_t$, and the initial stress at each strain level, $\sigma_0$, gives the stress relaxation ratio or stress...
ratio (Equation 3). Hence, this conversion makes it easier to make direct comparisons between different rubber compositions as they are now relative.

\[
\text{Stress ratio} = \frac{\sigma_t}{\sigma_0}
\]  

(3)

2.2.2 Dynamic test

Dynamic tests were carried out to determine the frequency dependent behaviour of the rubber materials. Virgin samples were utilised in this case because properties such as the dynamic stiffness are more accurate when there is minimal breakage of bonds from pre-stressing [11]. A servo-hydraulic testing machine Material Testing System (MTS) Multi-axis with a load cell of 25kN was used. The testing set up was similar with the previous tests by applying 120 grit emery paper to prevent sliding. The rubber samples were subjected to a strain amplitude of 10% at 4 different frequencies of 0.5 Hz, 1 Hz, 5 Hz and 10 Hz. The dynamic test was programmed using a MultiPurpose TestWare (MPT) integrated with a MTS Multi-axis testing machine.

2.2.2.1 Dynamic Stiffness

To calculate the dynamic stiffness of the rubber samples, the force amplitude applied, \( \ddot{F} \), is divided by the varying displacement amplitude, \( \ddot{y} \), at every antinode in the sinusoidal stress and strain response with respect to time (Equation 4). These values are then averaged out within each tested frequency.

\[
\text{Dynamic stiffness, } k_d = \frac{\ddot{F}}{\ddot{y}}
\]  

(4)

2.2.2.2 Phase Angle

The definition of the phase angle, \( \delta \), is shown in figure 4 where dynamic strain response lags behind the dynamic stress input.

![Figure 4. Dynamic stress input and strain response demonstrating phase lag [12].](image)

According to the Kelvin-Voigt model, the tangent of the phase angle is a factor of the damping coefficient, \( c \), elastic stiffness, \( k_s \), and frequency of harmonic input, \( \omega \) [13]. The elastic stiffness and input frequency are both known and the equation of motion is used to calculate the damping coefficient. Hence, we get the phase angle from equation 5 below:

\[
\text{Tan } \delta = \frac{cw}{k_s}
\]  

(5)
2.2.2.3 Damping Ratio
The damping ratio, $\xi$, is calculated from equation 6 below [13]:

$$\xi = \frac{W_L}{2n k' \bar{y}^2} \quad (6)$$

where,

$$W_L = \pi \bar{F} \bar{y} \sin(\delta) \quad (7)$$

The symbol, $k'$, represents the storage modulus of the sample which is similar to the stiffness of a rubberlike material. According to the ISO 6721-1 standard [14], it can be assumed to be equivalent to the dynamic stiffness for rapid stresses at low frequencies with reversible deformation. Hence, here it is assumed equal to the dynamic stiffness, $k_d$.

3. Results and Discussions

3.1 Static Compression Behaviour of Rubber Compounds
The stress strain responses of each rubber compound are compiled in figure 5. The uploading and unloading curves for all samples appear almost identical in behaviour and shape to each other. Carbon black is immediately observed to have a more significant response compared to the other rubber compounds and the hybrid filled rubber can be seen to already obey an incremental trend between themselves. The hybrid filled rubber samples show gradually increasing stress strain curves with respect to increasing ESP filler loading.

![Figure 5. Stress vs. strain responses for each rubber compound](image)

3.1.1 Maximum Compressive Stress at 40% Strain
The compressive stress experienced by the rubber compounds are an initial indication of the strength of samples. As shown in figure 6, it can be observed that the maximum compressive strength of the hybrid filled compounds are already higher than that of natural rubber. The hybrid filled rubber themselves follow an increasing trend in compressive stress as expected. There is a bigger gap in this trend between an ESP loading of 20 phr and 30 phr indicating the possibility of a larger increment in strength per content of filler used. However, carbon black is still observed to have the largest maximum compressive stress response as compared to the hybrid filled rubber.
3.1.2 Static Compression Stiffness

The third cycle static stiffness values under uniaxial compression testing is shown in Figure 7. Similar to the compressive stress, the results point towards an increasing pattern of static stiffness with increasing ESP content. Although the improvement in static stiffness of the rubber compound appears marginal at lower ESP content, the sudden increase between the results of OPA/ESP20 and OPA/ESP30 is also observed here. This could suggest an acceptable application of the hybrid rubber for lower magnitudes of force where the strength of carbon black is unnecessary and the bio-fillers present a more economical alternative. Additionally, increasing the loading of ESP could further improve the stiffness.

3.1.3 Hysteresis Loss Ratio

The effect of the hybrid fillers on the hysteresis ability of rubber is shown in Figure 8 for a constant 40% of strain. The reason the hysteresis loss ratio was not analysed at other amplitudes of strain was due to each sample being approximately 7.6mm to 8mm in depth. Testing the amplitude at 10%, for example, although significant in percentage, was not significant in absolute value and hence would not produce any discernible difference in results. On a smaller scale, the effect of this property is less prominent but has a significant difference on a larger scale. The hysteresis loss ratio of the hybrid filled rubber is lower compared to that of both natural rubber and carbon black rubber although this deficit is somewhat negated at 30 phr of eggshell powder. This could mean that any suitable applications would be more effective in smaller scaled pieces.
3.2 Stress Relaxation of Rubber Compounds

Figure 9 shows the stress relaxation response for OPA/ESP30. The regions of constant strain are discernible by a vertical drop in stress during the uploading and increase in stress during the unloading.

The time dependent behaviour of the rubber compounds in terms of the stress relaxation are shown in figure 10 (15% strain, uploading), figure 11 (30% strain, uploading), figure 12 (15% strain, unloading) and figure 13 (30% strain, unloading). The trends and behaviour of these results are consistent with the findings of [15]. In figure 10, the stress relaxation responses for the hybrid filled rubber are not observed to obey a pattern or trend of any sort between the two graphs. This effect is more pronounced at lower strain levels and at higher strain levels the stress relaxation curves seem to be almost identical. This similarity could be due to the material being more compact at higher strain levels and hence due to the physical thickness of the sample the effect was reduced slightly. For the unloading curves, the samples appear to obey a trend in relaxation with OPA/ESP10 generally having the fastest increase in stress and OPA/ESP30 having the slowest among the three hybrid samples.
Figure 12. Stress relaxation response during unloading for each rubber compound at 15% strain.

Figure 13. Stress relaxation response during unloading for each rubber compound at 30% strain.

All three hybrid samples appear to achieve equilibrium at almost the same time with each other for all cases with the exception of figure 10. The behaviours of both natural rubber and NR filled carbon black are consistent across all situations with NR filled carbon black achieving equilibrium the quickest in the uploading stage.

3.3 Dynamic Test
In general, the dynamic stiffness (figure 14), phase angle (figure 15) and damping ratio (figure 16) of the hybrid compounds do not appear to have a prominent difference between their magnitudes within each respective property. Increasing the loading of the hybrid filler does not seem to significantly affect the frequency dependency of the rubber. This can be seen where the trend lines for all compounds emerge very closely to each. It is not known if this is a phenomenon due to the type of filler used or if it is because the range of frequencies being tested is too small. Overall the dynamic analysis generally ranks the rubber samples in the following order carbon black > OPA/ESP30 > OPA/ESP20 > OPA/ESP10 > natural rubber with the carbon black being the most dynamically favourable.

Note there is a visible drop in properties at a frequency of 1 Hz across all five test samples in all three properties. It is a possibility that this is either a human or machine induced error as carbon black rubber does not undergo a transition phase at such a low frequency [17] and the drop is consistent for all compounds.

3.3.1 Dynamic Stiffness
The low gradient of the dynamic stiffness across the frequencies in figure 14 can be explained by rubberlike materials being expected to have minimal change in dynamic stiffness at “low” frequencies [18].
3.3.2 Phase Angle
In most cases, it is usually expected that the phase angle values across several frequencies will result in a flat line unlike the slope presented in Figure 15. However, it is not unusual to obtain experimental results that appear to have a slight increment in phase angle values with frequency [16].

Trends in phase angle values are generally used to determine transition regions within a specific material, hence, their magnitude is usually of less importance. However, as mentioned earlier, the phase angle also represents a sort of delayed displacement reaction of rubber when subjected to a force. Therefore, the position of the carbon black trend line above that of the hybrid fillers is a further indication of carbon black rubber having a higher stiffness although the actual magnitude would be better referred from stiffness calculations directly.

3.3.3 Damping Ratio
The results of the damping ratio are consistent with experimental works previously conducted [17]. The seemingly steep gradient is an expected occurrence even with small testing frequencies. The damping ratios of the hybrid fillers here are still compellingly lower than carbon black meaning either the damping ability of the hybrid samples are very limited or their critical damping coefficients are rather large. Rubber filled carbon black still maintains better overall damping with respect to the
critical damping coefficient (damping ratio) and appears to actually have a damping ratio increment per increment in frequency, albeit a small one.

![Graph showing damping ratio against frequency for each rubber compound.]

**Figure 16.** Damping ratio against frequency for each rubber compound.

4. Conclusion
Based on the results of static compression tests, it does not suggest that the hybrid bio-fillers have a significant advantage over rubber filled carbon black even though they do indeed have substantial mechanical and dynamic properties. Stress relaxation results do not contribute at any potential over rubber filled carbon black and there is actually a great deal of difference in this property. Across all dynamic applications, content of loading does not seem to significantly affect the dynamic properties. While the dynamic properties could be considered at a scalable magnitude with increasing frequency, the hybrid bio-fillers appear to be at a disadvantage again. The rubber with OPA/ESP content does not affect the dynamic properties of the hybrid filled rubber significantly, hence a lower content could be used for a range of vibrational scenarios.

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6. References
[1] J. M. Kelly and D. Konstantinidis 2011 *Mechanics of Rubber Bearings for Seismic and Vibration Isolation*. Somerset Wiley p 1
[2] R. M. Gibbons 1986 Silicon rubber gasket and material *Google Patents* p 2
[3] International Carbon Black Association 2016 *Carbon Black User’s Guide* p 36
[4] T. Amari, N. J. Themelis, and I. K. Wernick 1999 Resource recovery from used rubber tires *Resour. Policy* vol 25 no. 3 pp 179–188
[5] Y. Fang, M. Zhan, and Y. Wang 2001 The status of recycling of waste rubber *Mater. Des.*, vol 22 no. 2 pp 123–128
[6] Z. X. Ooi, H. Ismail, and A. A. Bakar 2013 Optimisation of oil palm ash as reinforcement in natural rubber vulcanisation: A comparison between silica and carbon black fillers *Polym. Test.* vol. 32 no. 4 pp 625–630
[7] S. Lumlong, S. Wanapan, B. Khamsri, and P. Pungpo 2016 Effect of Eggshell as a Filler on Rubber Composite Properties
[8] A. S. M. Bashir, Y. Manusamy, L. C. Thiam, H. Ismail, and S. Ramasamy 2017 Mechanical, Thermal, and Morphological Properties of (Eggshell Powder)-Filled Natural Rubber Latex Foam *J Vinyl Addit. Technol*, no. 23 pp 3–12
[9] L. Kari, P. Eriksson, and B. Stenberg 2001 Dynamic stiffness of natural rubber cylinders in the audible frequency range using wave guides Kautschuk Gummi Kunststoffe vol. 54 no. 3 p 106

[10] R. Houwink and H. K. De Decker 1971 Elasticity, plasticity and structure of matter. Cambridge University Press p 1

[11] Y. Zhou, J. Wang, H. Chen, Q. Nie, Q. Sun, and Y. Wang 2009 The influence of pre-stressing on breakdown characteristics in liquid silicone rubber J. Electrostat. vol 67 no. 2–3 pp 422–425

[12] G. W. Ehrenstein, G. Riedel, and P. Trawiel 2004 Chapter 6 Dynamic Mechanical Analysis Therm. Anal. Plast. Theory Pract. pp 236–299

[13] E. J. Graesser and C. R. Wong 1991 The Relationship of Traditional Damping Measures for Materials with High Damping Capacity pp 1-3

[14] B. ISO,6721-1: 2011 Plastics Determ. Dyn. Mech. Prop. Gen. Princ.

[15] M. Cespi, G. Bonacucina, M. Misici-Falzi, R. Golzi, L. Boltri, and G. F. Palmieri 2007 Stress relaxation test for the characterization of the viscoelasticity of pellets Eur. J. Pharm. Biopharm. vol. 67 no. 2 pp 476–484

[16] M. Abdelmouleh, S. Boufi, M. N. Belgacem, and A. Dufresne 2007 Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading Compos. Sci. Technol. vol 67 no. 7–8 pp 1627–1639

[17] A. I. Medalia, 1978 Effect of Carbon Black on Dynamic Properties of Rubber Vulcanizates Rubber Chem. Technol. vol 51 no 3 pp 437–523