Effect of Different Types of Rubbers and Carbon Black Grades on Curing Characteristics and Dynamic Properties for Anti-vibration Application

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Abstract. Nowadays, the automotive industry is facing a major challenge to meet the changing demand on performance, material specifications and durability requirements. An anti-vibration part is a critical component in automotive, used to eliminate the vibration. In order to produce a good anti-vibration component, the rubber compound needs to be formulated with good damping properties. This research work focused on the effect of (unfilled) rubber types; natural rubber (SMR 60CV, SMR L, RSS) and synthetic rubber (SBR, NBR, CR, EPDM) and the effect of carbon black grades (N220, N330, N550, N774, N990). The curing characteristics and dynamic properties (dynamic stiffness, $K_d$) at 15, 45 and 100 Hz were analyzed. The curing characteristic results showed there is a relationship between both factors. The longer cure time for types of rubber indicates longer time is needed to break higher bond energy of the rubber chain. Meanwhile, for carbon black grades, the cure rate is gradually increased with lower carbon black surface area due to the diffusion limitation and lower chain mobility. The dynamic properties results were based on the Payne effect theory which influenced by the rubber bond structure that gave higher value of dynamic stiffness due to rubber-rubber interaction. For carbon black grades, the higher surface area of carbon black gave higher dynamic stiffness due to increased rubber-filler and filler-filler interactions.

1. Introduction

The automotive or also known as automobile industry is directly related to the rubber industry. There are various components or parts made from rubber used in automobiles including the high-technology adhesive and sealant products required by the aerospace and other demanding applications in automobiles and automotive industries. One of the most critical rubber products is mainly related to the dynamic application for example an anti-vibration component usually used for shock absorption [1].

A rubber-based anti-vibration component is widely used with the following main objectives; to eliminate harmful vibration, reduce noise and absorb shock [2]. Rubber is used as anti-vibration based on its good vibration-absorbing characteristic which reduces the effect of running engines, ensuring smooth humming for automotive anti-vibration components. The high internal isolating properties of rubber particularly contribute as anti-vibration components [3]. Some examples of the anti-vibration components for automotive application are; rubber bushing, damper, engine mounting, exhaust hanger and others. There are several commonly used rubbers for the anti-vibration application including natural rubber (NR), chloroprene rubber (CR), styrene butadiene rubber (SBR), ethylene propylene diene monomer (EPDM) [4, 5].

The most common way of reducing unwanted vibrations at a receiving structure in between the source and receiver, is either to reflect the vibration energy by significantly dissipate or changing the impedance through induction of additional damping, [6]. The dynamic motion in anti-vibration application is correlated to the dynamic properties of the rubber compound as it
responds to the periodic forces applied during application which do not cause failure. The dynamic properties of anti-vibration components are referring to the viscoelasticity properties of the rubber compound. Different types of rubbers contribute to different viscoelastic properties. Selecting a right type of rubber can produce a good anti-vibration component as it refers to the compound stiffness and viscoelastic properties [6]. The dynamic properties of rubber compounds are also contributed by the type of carbon black. The effect of different carbon black fillers on the dynamic properties of a given rubber and cure system, filler networks and strength, are the main parameters that govern the behavior of the filled rubber. The thermodynamic and kinetic of carbon black filler network formation is related to filler-filler, rubber-filler, as well as rubber-rubber interactions that also known as the Payne effect theory [7].

In automotive engineering application, rubber is an efficient material to be used as anti-vibration component due to its properties. However, designing a right rubber formulation to meet critical product specifications such as dynamic and damping properties was deemed difficult. Although there are many previous research studies on the effect of rubber and carbon black types, the studies however were found to be limited to the general mechanical properties and lesser works were reporting on the dynamic stiffness (Kd) using single-bonded rubber. Besides, the influence of the stiffness test of rubber compound towards noise and vibration has also become a concern. Due to the limitation of study on dynamic properties in designing rubber anti-vibration, this research work is conducted to study the effect of rubber types and carbon black grades on the dynamic properties for rubber anti-vibration application by using single-bonded rubber following JIS K6394 (N2 type).

2. Materials and Methods
In this work, purchases of the natural rubbers (SMR 60 CV, SMR L RSS) were made from Mardec Berhad and the synthetic rubbers (SBR, NBR, CR, EPDM) from Imago Chemical's Sdn. Bhd. All the carbon black grades were purchased from Cabot Cans Sdn. Bhd. This research works were divided into two series; (i) unfilled and (ii) filled rubber compounds. The first series (unfilled rubber compounds) were used to study the effect of different types of rubbers (NR, SBR, NBR, CR and EPDM) on the cure characteristics and dynamic stiffness properties. The second series (filled rubber compounds) were used to analyze the effect of different types of carbon black grades (N220, N330, N550, N774 and N990) with 50 phr of carbon black loading on the cure characteristics and dynamic stiffness properties of rubber compounds. Both of these series used semi-efficient sulphur vulcanization (semi-EV) system. Materials and formulations used in this study are tabulated in Table 1 (unfilled) and Table 2 (filled).

The rubber compounds were prepared according to ASTM D3184-89 using laboratory size two-roll mill machine model XK-160. After compounding process, the curing characteristics of rubber compounds were carried out by using an oscillating die rheometer tester (ODR 2000) according to ASTM D2084 with the temperature of 165 °C. The dynamic test (dynamic stiffness, Kd) was conducted on single rubber bonded according to JIS K6394 (N2 type) by using Servopulser testing machine at a control temperature of 23 ± 2 °C and the results were plotted at 15, 45 and 100 Hz.
### Table 1. The rubber formulations for first series (unfilled) rubber compounds

| Ingredients | SMR 60CV | SMR L | RSS | SBR | NBR | CR | EPDM |
|-------------|----------|-------|-----|-----|-----|----|------|
| SMR 60CV    | 100      | -     | -   | -   | -   | -  | -    |
| SMR L       | -        | 100   | -   | -   | -   | -  | -    |
| RSS         | -        |      | 100 | -   | -   | -  | -    |
| SBR         | -        | -    | -   | 100 | -   | -  | -    |
| NBR         | -        | -    | -   | -   | 100 | -  | -    |
| CR          | -        | -    | -   | -   | -   | 100| -    |
| EPDM        | -        | -    | -   | -   | -   | -  | 100  |
| Zinc oxide  | 5        | 5    | 5   | 5   | 5   | 5  | 5    |
| Stearic acid| 1        | 1    | 1   | 1   | 1   | 1  | 1    |
| Sulphur     | 1.5      | 1.5  | 1.5 | 1.5 | 1.5 | 1.5| 1.5  |
| CBS         | 2        | 2    | 2   | 2   | 2   | 2  | 2    |
| TMTD        | 1        | 1    | 1   | 1   | 1   | 1  | 1    |

*phr = part per hundred rubber

### Table 2. The rubber formulations for second series (filled) rubber compounds

| Ingredients | N220 | N330 | N550 | N774 | N990 |
|-------------|------|------|------|------|------|
| SMR 60CV (Rubber) | 100  | 100  | 100  | 100  | 100  |
| N220        | 50   | -    | -    | -    | -    |
| N330        | -    | 50   | -    | -    | -    |
| N550        | -    | -    | 50   | -    | -    |
| N774        | -    | -    | -    | 50   | -    |
| N990        | -    | -    | -    | -    | 50   |
| Zinc oxide  | 5    | 5    | 5    | 5    | 5    |
| Stearic acid| 1    | 1    | 1    | 1    | 1    |
| Sulphur     | 1.5  | 1.5  | 1.5  | 1.5  | 1.5  |
| CBS         | 2    | 2    | 2    | 2    | 2    |
| TMTD        | 1    | 1    | 1    | 1    | 1    |

*phr = part per hundred rubber

### 3. Results and Discussion

In this research work, all the rubber compounds used similar types of cure system which is semi EV system sulphur vulcanization. The scorch time ($t_{s2}$) and cure time ($t_{c90}$) results were plotted in Fig. 1. The results showed that both $t_{s2}$ and $t_{c90}$ values gave no significant difference for NR compounds due to similar rubber structure which is polyisoprene. For synthetic rubber, CR showed the lowest $t_{s2}$ followed by NBR, SBR and EPDM due to their average bond energy. As the vulcanization process is the breakage of rubber chain, therefore molecules with the higher bond energy need higher energy to be broken [8]. Longer cure times indicated longer times needed to break higher bond energy of the rubber chain. For carbon black grades effect, the vulcanization rate was gradually increased with the decreased surface area of carbon black. This may be due to the diffusion limitation and lower chain mobility of rubber introduced by the carbon black-rubber interactions [9].
By referring to Fig. 2, the Kd results at 15, 45 and 100 Hz were plotted for rubber type and carbon black grade effect. Higher Kd values with respect to EPDM and SBR are due to the high bond energy of diene and styrene bulky groups attached at the rubber backbone chain, requiring a higher energy for the occurrence of bonding breakage. Hence, it restricted the molecular chain orientation. While for NBR rubber, high Kd values is due to the strong C≡N bond in the rubber structure where it needed high energy to break. The C-Cl side chain bond in CR rubber has also increased the bond energy. However, in NR compounds, the polyisoprene rubbers with empirical formula (C\(_5\)H\(_8\))\(_n\) are essentially hydrocarbons consisted of only carbon and hydrogen elements which are also inherent in other rubber structures. Increasing frequency has decreased the dynamic stiffness for all rubber compounds due to the increased in rubber chain movement thus leads the molecules to slip past one another and sometimes even bond breakage occurred [10].
The highest surface area of carbon black increased the Kd values due to the increased interactions between rubber-filler and filler-filler. The rubber-filler interaction includes physical absorption of the rubber chains on the carbon black filler surfaces [11]. This interaction restricted the rubber chain mobility on the filler surfaces (Payne theory). Increment of the Kd values succeeding frequency amplification may be due to elevation in the energy absorption through a viscous flow of the rubber matrix and the interfacial interaction between the filler and rubber matrix. This absorption might be due to the overcoming inter-particles interaction by the van der Waals forces.

**Fig. 2.** The dynamic stiffness, Kd at 15, 45 and 100 Hz for different types of rubbers and carbon black grades.
4. Conclusions

Based on this research work, it can be observed that different types of rubber compounds gave significant effect on the cure characteristics. Higher values of $t_{c2}$ and $t_{c90}$ were due to the bulky group attached at the rubber backbone chain. This bulky group tends to hinder the chain mobility, thus higher energy was needed to break the bond. The Kd test was related to the Payne effect behavior which depends on the viscoelasticity and crosslinking of the rubber itself. The differences in carbon black grades were clearly affecting the cure characteristics of the rubber compounds. The vulcanization rate was gradually increased with reduction of the carbon black surface area due to limitation in diffusion and lower chain mobility of the rubber compounds. Larger carbon black surface area would strengthen the interactions between rubber-filler and filler-filler, thus leads to increment in the Kd values.

References

[1.] Oshima H, Aono Y, Noguchi H and Shibata S 2007 Fatigue characteristics of vulcanized natural rubber for automotive engine mounting (characteristics of composition and mechanical properties) Memoirs of the faculty of Engineering, Kyushu University 67(2)

[2.] Kurna S, Jain R, Mathur A, Parwal M and Legala A 2017 Design Optimization of Engine Mounts for Commercial Vehicle Application to Avoid Failures. SAE Technical Paper (No. 2017-26-0287)

[3.] Zhou X Q, Yu D Y, Shao X Y, Zhang S Q and Wang S 2016 Research and applications of viscoelastic vibration damping materials: a review. Compos. Structures 136, 460-480

[4.] Phu P Q and Nguyen Khac Tien L T H 2017 Effects of sevral factors on anti-vibration ability of EPDM rubber J. Sci Technol. 55(1B) 202-207

[5.] Li Q, Zhao J C and Zhao B 2009 Fatigue life prediction of a rubber mount based on test of material properties and finite element analysis engineer. failure analysis 16(7), 2304-2310

[6.] Sjoberg M 2002 On dynamic properties of rubber isolators (Doctoral dissertation, Institutionen för farkossteknik)

[7.] Wang Z, Li S, Wei D and Zhao J 2015 Mechanical properties, Payne effect, and Mullins effect of thermoplastic vulcanizates based on high-impact polystyrene and styrene-butadiene rubber compatibilized by styrene-butadiene-styrene block copolymer. J. Thermoplast. Compos Mater. 28(8)1154-1172

[8.] Agrawal C M, Ong J L, Appleford M A and Mani G 2013 Introduction to Biomaterials: Basic Theory with Engineering Applications. Cambridge University Press.

[9.] Salehi M M, Khalkhal T, Solevman R and Barari M 2016 Effect of carbon black type on the thermal properties of fluorooelastomer European J. Adv. Eng. Technol. 3(2) 27-30

[10.] Geethamma V G, Asaletha R, Kalarikkal N. and Thomas S 2014 Vibration and sound damping in polymers Resonance 19(9) 821-833

[11.] Shuib R K and Pickering K L 2016 Effect of Carbon Black on the Dynamic Properties of Anisotropic Magnetorheological Elastomer J. Eng. Sci. 12(1)