The Influence of Different Types of Rubber on Curing Behaviour and Dynamic Properties of Rubber Compound

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Abstract. The aim of the present work is to investigate the effect of the different types of rubber on cure characteristics. The paper also explores the dynamic properties of these rubbers. The curing behaviour of the rubber compound is the main consideration for the rubber moulding process maker, which govern the process and properties of the rubber product. The dynamic properties are another factor that needs to take into account as it is the important properties especially in designing an anti-vibration component. Three types of rubber were used includes natural rubber (NR), styrene butadiene rubber (SBR) and chloroprene rubber (CR). All rubber compounds were prepared based on semi-efficient (semi-EV) sulphur vulcanization system. These compounds were mixed by melt mixing on a two-roll-mill lab scale machine. The cure characteristics were analysed using the Moving Die Rheometer (MDR 2000). The results obtained show that SBR presented higher torque difference (MH-ML) value followed by NR and CR. The hardness of the rubber compound showed a similar trend as torque different result. The dynamic properties; static stiffness, Ks and dynamic stiffness, Kd were tested using the Selvopulser Testing machine. For Kd value, the test was reported on the frequency of 100 Hz. The static stiffness, Ks shows a similar trend as the torque different and hardness results; SBR>NR>CR however, for dynamic stiffness, Kd value trend has shown significant changed to SBR>CR>NR. This is due to the bond breakage in a rubber chain also known as Payne effect. In conclusion, the Kd, torque different and hardness are correlated to the rubber molecular weight, meanwhile, for Ks is much more related to interaction of molecular structure in rubber compound (Payne effect).

1. Introduction

Rubber materials have been widely used in automotive engineering application nowadays. Rubber has found an indisputable role in many mechanical applications for example tires, seals, hoses and in automotive industries. Vibration is normally conceived as unwanted dynamic motions in mostly vehicle application and great effort is made reducing these motions and to increase vehicle component durability [1]. The rubber properties being generally soft while showing large inherent damping that make the material a perfect choice for use in vibration application. The viscoelastic behaviour of rubber material is the reasons for this usage.

The selecting the right rubber is very important as it is the main contribution of the elastic properties of end rubber products. The most commonly used rubber for the dynamic application is natural rubber (NR) due to its elastic properties. However, NR is known for poor ageing properties, chemical resistance and ozone resistance. Nowadays, the synthetic rubber has been also used in rubber automotive...
application such as Styrene Butadiene Rubber (SBR) due to its excellent abrasion resistance and Chloroprene Rubber (CR) due to its good ageing resistance, high ozone and weather resistance. Hence, the understanding of viscoelastic behaviour and rubber properties is essential for the efficient use and proper design of these materials for automotive engineering application [2] [3].

Although there were many studies on the effect of rubber types, those studies are only limited to the mechanical properties and fewer on static and dynamic stiffness. Besides that, the influences of stiffness test of rubber compound towards noise and vibration also become a concern. Thus, the present study focuses on the influence of different rubber types on curing characteristic and dynamic properties in term of static stiffness and dynamic stiffness based on NR, SBR and CR rubber compounds are discussed in this paper.

2. Experimental study
This work aimed to examine the influenced of different types of rubber; NR, SBR, and CR on the curing behaviour and dynamic properties for dynamic application of rubber products.

2.1 Material
There were three types of rubber used in this study; natural rubber (NR), styrene butadiene rubber (SBR) and Chloroprene rubber (CR). NR is Malaysian rubber (SMR 20 CV) supplied by Mardec Berhad. SBR (Nipol 1502) supplied by Centre West Industrial Supplies Sdn. Bhd., and CR (Bayprene 210) supplied by Imago Chemicals Sdn. Bhd. Table 1 shows the formulation used in this study. Other compounding ingredients such as zinc oxide, stearic acid, sulphur, N-cyclohexyl-2-benothiazole sulphenamide (CBS) and tetramethylthiuram disulphide (TMTD) were purchased from Anchor Chemical Co. Compounding process was carried out in accordance with ASTM D 3184-89 using two-roll-mill.

Table 1. Rubber compound formulation

| Material  | Part per hundred rubber (phr) |
|-----------|-------------------------------|
| Rubber *  | 100                           |
| Zinc oxide| 5                             |
| Stearic acid | 1                           |
| Sulphur   | 1.5                           |
| CBS       | 2                             |
| TMTD      | 1                             |

* NR/SBR/CR

2.2 Cure characteristics
The cure characteristics were studied using the Mosanto Moving Die Rheometer (MDR 2000) according to the ASTM D 2084. About 4 grams of the respective compound samples were tested at the vulcanization temperature of 165°C.

2.3 Vulcanization process
Rubber button with respectively ~12 mm thickness was compression moulded at 165°C using hot press according to respective cure times, $t_{90}$, determined with the MDR 2000. For the vulcanization of static and dynamic stiffness, the dimension of the specimen was followed JIS K 6394 in the classification of N2 type. The hardness test was carried out, followed by standard ASTM D 2240, type Shore A.
2.4 Static and Dynamic stiffness study

For the stiffness test (static and dynamic), the testing was conducted, followed by standard JIS K 6394 with N2 type dimension specimen. Both tests were tested using a Servopulser testing machine at the test temperature of 23 ± 2 °C. The static stiffness test (Ks), first it undergoes the preload from 0 to 3.2 mm. The Ks value was measured at 1 mm to 2 mm (slope of force over displacement) under the compression mode. For dynamic stiffness test (Kd) also undergo the preload test before proceeding to the actual test. The Kd values were measured from sine swept frequency 0 Hz to 100 Hz using the amplitude of ± 0.05 mm under compression and tension mode and the reported value was at the frequency of 100 Hz.

3. Results and discussion

3.1 Cure characteristics and hardness

Figure 1 shows the torque different value (MH-ML) for NR, SBR and CR. It can be observed that SBR gave highest torque different value, followed by NR and CR. The trend might be due to the modulus and rigidity of each rubber. The SBR shows slightly higher than NR due to the pendant group that attaches to the backbone chain which is styrene bulky group. This bulky group of styrene will restrict the mobility of the polymeric chain by preventing the chains from sliding past each other easily, hence resulted in increasing the glass transition temperature thus increase the modulus [4].

In the comparison of synthetic rubber; SBR has higher in molecular weight which is ~158.244 g/mol compared to CR is ~ 88.534 g/mol. Based on Figure 1, the torque difference is about 50 % for SBR and CR. The higher molecular weight will increase the rubber modulus thus increase in torque different [5]. Even though NR has lower molecular weight than CR which is 68.12 g/mol, but the torque different is higher for NR. This might be due to the dirt contained in natural rubber which is produced from cup lump. This can be correlated to the Mooney of viscosity for each rubber which is 67 MU for SBR, 62 MU for NR and 49 MU for CR.

By referring Table 2, the scorch time (ts2) for each rubber compound, SBR obtained higher ts2 value followed by a CR and NR. The ts2 is known as the time from the beginning of the test to the time the torque has increased 2 units above ML value. It shows at which point the vulcanization (curing) actually starts. The vulcanization is a process that converts rubber or elastomer into the cross-linked polymer by forms bridges between individual polymer molecules when temperature is applied [6-7]. In this study, the vulcanization agent used is sulphur. The process starts with a polarized sulphur molecule or with a sulphur cation reaction with rubber polymer chain. The breakage of polymer bond is needed in order to form a sulphur cross-linked in the polymer chain with higher energy is required to break the higher bond energy. The presence of the styrene bulky group in SBR required higher energy to break the bond followed by CR which consists of C-Cl bond and C-C bond in NR. In this case, the similar temperature was used for vulcanization process and the rheometer. The longer time observed due to the time required to break higher bond energy. Thus, SBR showed longer scorch time and cure time tc90 (time of 90% cure).

Table 2. Cure characteristic for NR, SBR and CR rubber compounds

| Cure characteristic | Type of rubber |
|---------------------|----------------|
|                     | NR  | SBR | CR  |
| ts2, min           | 1.45| 2.10| 1.87|
| tc90, min          | 1.92| 3.07| 2.92|
Figure 1. The torque different value for NR, SBR and CR

By referring Figure 2, its show the similar trend as torque different. As known that, hardness measure the resistance of material to deformation under compression load and dependent on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity and viscosity. When the compound is hard, it needs to obtain higher stress and lower strain in the stress-strain curve. Due to this, it will show the higher value of the slope (stiffness). The stiffness of the material is the amount needed to deform when force is applied. The higher force will give higher in hardness value. The torque different (MH-ML) can be correlated to the hardness and modulus [8]. Thus, the higher torque different material gives higher value in hardness.

Figure 2. The hardness values for NR, SBR and CR
3.2 Static, Ks and dynamic, Kd stiffness study

Stiffness can be related to the rigidity of the rubber compound as its measure the force over deflection. The effect of different rubber on static, Ks and dynamic, Kd stiffness are shown in Figure 3. It can be observed that for static stiffness, Ks, the trend is clearly followed the hardness result. The higher value is observed for SBR followed by NR and CR. This might be due to the similar testing mode which is in compression mode for both tests. As discussed before, the bulky pendant group of styrene in SBR will increase the rubber modulus and rigidity, while for NR the linearity of the polysisoprene molecular structure gave higher Ks value compared to the CR. Besides that, the molecular weight of rubber also the main contribution for the rubber modulus [4]. Thus, the higher in molecular weight of SBR that consists of pendant bulky group gave higher in Ks value followed by NR and CR.

However, for dynamic stiffness, Kd test, (refer Figure 3) the result shows that the higher Kd value obtained for SBR followed by CR and NR. It can be observed that the Kd trend does not follow the Ks and hardness trend. This might be due to the different mode test of Ks and hardness compared to Kd test which is compression and tension mode (cyclic loading condition) test at the certain frequency. The dynamic stiffness calculation is based on the combination of viscous and elastic stiffness [9]. The dynamic stiffness is a particular feature of the stress-strain behaviour of rubber. This behaviour is also known as the Payne effect [10]. The effect is observed under cyclic loading conditions with small strain amplitude and is manifest as a dependence of the viscoelastic storage modulus on the amplitude of the applied strain.

Physically, the Payne effect can be attributed to deformation-induced changes in the materials microstructure for example to breakage and recovery of weak physical bond linkages. It depends on the filler content on the material and disappears for the unfilled elastomer. For this study, the rubber-rubber interaction only being considered because of the used of only unfilled rubber compounds.

**Figure 3.** The effect of static, Ks and dynamic, Kd stiffness for each rubber

The higher of bond energy of the styrene bulky group attach at a rubber backbone chain in SBR required higher energy to break the bond and this will contribute the higher value of Kd. While for CR is due to the side chain of C-Cl with the bond energy of 339 kJ/mol. For NR, the polysisoprene structure only consists of carbon and hydrogen, which also similar to SBR and CR structure. Due to this bond energy in rubber chemical structure, the higher Kd value obtained for SBR is due to the styrene bulky group
bond energy, followed by CR and NR. Thus, the stronger the bonding energy of rubber polymer chain, the higher the rubber stiffness.

4. Conclusion

In conclusion, the curing characteristic which is torque different (MH-ML) can be used to predict static stiffness, $K_s$ value as it shows a similar trend. This also can be correlated to the hardness of rubber compound. While, for dynamic stiffness, $K_d$, the main contribution is the molecular structure of rubber as it is related to the viscoelasticity of rubber as stated in the Payne effect. In this study, Payne effect focuses on the rubber-rubber interaction. Higher the bond energy interaction in rubber molecular structure will need higher energy to break the bond structure. Higher energy can be referred to the force applied. By referring back to the stiffness calculation which is the force over deflection, thus it gives higher in $K_d$ value.

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