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Influence of Sulfur Ratio to Accelerator on the Crosslink Density, Mechanical, Dynamic, and Damping Properties of Unfilled Natural Rubber Vulcanizate

Adi Cifriadi[1,2], Purwantiningsih Sugita[1*], Tetty Kemala[1], Siti Nikmatin[3]

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia

[2] Indonesian Rubber Research Institute, Palembang, Indonesia

[3] Department of Physics, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia

Abstract: Natural rubber (NR) is a biopolymer with low vibration damping capacity. NR requires modification of its viscoelastic properties through crosslink in NR vulcanizates molecular chains as vibration damping. This study is the first to report a correlation between crosslink density and dynamic shear properties of NR vulcanizates, including hysteresis loop area, shear stiffness, equivalent damping ratio, and effective shear modulus. This correlation is necessary to develop NR vulcanizates properties appropriate to the vibration isolator product requirement. This research also reveals the rubber compound formulation technique to achieve the optimum value of the viscoelasticity and damping properties of NR vulcanizates by setting the crosslink density. In addition, this research investigates the influence of sulfur ratio to MBTS accelerator on the crosslink density, mechanical, dynamic, and vibration damping properties of unfilled NR vulcanizates. The crosslink density of unfilled NR vulcanizates is determined by the Mooney-Rivlin method. At the same time, the dynamic properties and vibration damping were evaluated by testing the dynamic shear properties. Testing results showed that the increment of sulfur to MBTS accelerator ratio increased crosslink density value. The highest crosslink density was measured at a 7.16 x 10-5 mol/cm3 obtained by NR vulcanizates containing sulfur to MBTS accelerator ratio at 2.15. This ratio also produced optimum value for mechanical properties (tear and tensile strength), elastic properties (compression set, LUPKE rebound resilience, and elastic modulus), and the highest effective shear modulus value. The value of tear strength, tensile strength, compression set, LUPKE rebound resilience, elastic modulus, and an effective shear modulus were 28.5 N/mm; 25.2 MPa; 3.65%; 79; 3.89 MPa, and 0.169 MPa. The optimum value of vibration damping was obtained at 1.39% of an equivalent damping ratio produced by NR vulcanizates containing sulfur to MBTS accelerator ratio at 0.14.

Keywords: natural rubber, sulfur ratio to the accelerator, crosslink density, mechanical properties, dynamic properties.

硫与促进剂之比对未填充天然橡胶硫化胶交联密度、力学、动态和阻尼性能的影响

摘要：天然橡胶是一种具有低振动阻尼能力的生物聚合物。天然橡胶需要通过交联来改变其粘弹性能 天然橡胶硫化分子链作为减振。本研究首次报道了交联密度与天然橡胶硫化胶动态剪切性能之间的相关性，包括滞后回线面积、剪切刚度、等效阻尼比和有效剪切模量。这种相关性对于开发适合隔振器产品要求的天然橡胶硫化物性能是必要的。该研究还揭示了通过设置交联密度来实现天然橡胶硫化胶粘弹性和阻尼性能的最佳值的胶料配方技术。此外，本研究还研究了硫比与苯并噻唑二硫化物促进剂对未填充天然橡胶硫化胶交联密度、机械、动态和减振性能的影响。未填充天然橡胶硫化胶的交联密度由穆尼-里夫林法测定。同时，通过测试动态剪切性能来评估动态性能和减振性能。测试结果表明，硫与苯并噻唑二硫化物促进剂比例的增加增加了交联密度值。在 7.16x10-5 摩尔/立方厘米下测得的最高交联密度是

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About the authors: Adi Cifriadi, Department of Chemistry, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia; Indonesian Rubber Research Institute, Palembang, Indonesia; Purwantiningsih Sugita, Tetty Kemala, Department of Chemistry, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia; Siti Nikmatin, Department of Physics, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia

Corresponding author Purwantiningsih Sugita, purwantiningsih@apps.ipb.ac.id

由含硫与二硫化苯并噻唑促进剂比率为 2.15 的天然橡胶硫化胶获得的。该比率还产生了机械性能（撕裂和拉伸强度）、弹性性能（压缩永久变形、卢普克回弹性和弹性模量）和最高有效剪切模量值的最佳值。撕裂强度、拉伸强度、压缩永久变形、卢普克 E 回弹性、弹性模量和有效剪切模量的值为 28.5 牛/毫米；25.2 兆帕；3.65%；79; 3.89 兆帕和 0.169 兆帕。在含硫天然橡胶硫化橡胶与二硫化苯并噻唑促进剂之比为 0.14 的等效阻尼比为 1.39% 时，获得了最佳减振值。

关键词：天然橡胶、硫与促进剂的比例、交联密度、机械性能, 动态性能。

1. Introduction

Most elastomeric engineering materials for vibration isolators need mechanic, elastic, and damping properties to fulfill the product requirements. Rubber is generally good for vibration damping material. The vibration damping capacity of rubber materials varies widely, and it is usually influenced by its viscoelastic properties [1, 2, 8]. In general, butyl rubber is a synthetic rubber that has the best vibration damping capacity, while the natural one is classified as having a lower vibration damping capacity [3]. The tangent delta value (loss factor) indicates that the vibration damping capacity of natural rubber is lower than that of synthetic one [3]. Some studies on increasing the vibration damping capacity of natural rubber have been carried out by increasing the stiffness or changing the viscoelastic properties [4-11]. The research was carried out to obtain a vibration-damping capacity that meets the requirements for applications in machinery, automotive, or earthquake-resistant buildings.

The chemicals used in manufacturing rubber compounds improve elasticity and strength, especially for crosslinking materials or vulcanizing agents [12-21]. Nabeel Alshabatat and Ahmad Abouel-Kasem [14] stated that sulfur is the most widely used crosslinking material for unsaturated elastomer, with a carbon-carbon double bond in its molecular structure, such as natural rubber. The crosslinks formed in the sulfur vulcanization system are sulfide crosslinks greatly influenced by the sulfur ratio to the accelerator [12-15, 19-21]. In the sulfur vulcanization system, the formation of sulfide crosslink depends on the sulfur ratio to the accelerator, temperature, and vulcanization time [19, 20]. The sulfur ratio to accelerator added to rubber compounds can set the amount and type of sulfide crosslinking in the rubber molecules [13, 19]. The types of sulfide crosslink formed include monosulfide crosslink, disulfide crosslink, or polysulfide crosslink [13, 14, 17, 19, 21].

The number and types of monosulfide, disulfide, and polysulfide crosslinks can influence the mechanical properties of rubber products [13, 14, 17, 19, 21]. The crosslink density shows the number of crosslinks formed on rubber macromolecules during the vulcanization process. The density of sulfide crosslink significantly influences the mechanical properties of the resulting vulcanizate [12-15, 17, 19, 20]. The formation of crosslinks in this vulcanization process can increase material elasticity and strength [19, 22-24]. The emergence of hysteresis indicated by the ratio between the viscous and elastic components of the material deformation resistance is also affected by the crosslinks number. Generally, the higher the crosslinks formed, the lower the hysteresis value [25]. Therefore, this research will study the relationship of variations in the sulfur ratio to the accelerators on the crosslink density, mechanical, elastic, viscoelastic, and vibration damping properties of NR vulcanizate for rubber compound formulation vibration isolator.

2. Material and Methods

2.1. Research Materials

The rubber compound production requires natural rubber type SIR 20 as a base elastomer, an activating agent in the form of zinc oxide (ZnO) UN 3077 from Lanxess Germany, stearic acid Aflux®52 from Lanxess Germany, an accelerator in the form of 2-2'-dithiobenzothiazole (MBTS) of Kemai brand from China, and vulcanizing material in the form of sulfur (Midas SP 325 produced by Miwon Co Japan). The rubber compound chemicals used are entirely at the technical quality level. The rubber compound formula applied in this experiment is designed at various doses of sulfur for the MBTS accelerator, as shown in Table 1.

Table 1 Natural rubber compound formula

Sample Code	NR (% Wt)	ZnO (phr)	Stearic Acid (phr)	Sulfur (phr)	MBTS (phr)	Ratio (Sulfur/MBTS)
A1	100	5	2	0.20	1.45	0.14
A2	100	5	2	0.24	1.41	0.17

Continuation of Table 1						
A3	100	5	2	0.30	1.35	0.22
A4	100	5	2	1.50	1.35	1.11
A5	100	5	2	2.90	1.35	2.15

Note: The amount of these additives to be added is expressed in parts per hundred rubber (phr).

2.2. Rubber Compound Production

The rubber compound is made by mixing rubber with some chemicals in a laboratory-scale open mill with a capacity of 1000 g/batch with the German brand, Bernstorff. The rubber compound production refers to the ASTM 3182 standard with the mixing stages shown in Table 2. First, natural rubber is masticated until its viscosity level drops significantly so that it is easier to mix it with the chemicals. Then, masticated natural rubber becomes softer, characterized by its plasticity level. Next, the rubber compound chemicals are added to natural rubber in the order of ZnO, stearic acid, MBTS, and the last is sulfur. After all the rubber compound chemicals have been added, the rubber is continuously grounded and homogenized.

Table 2 Procedure for mixing natural rubber compounds

Stage	Process or Ingredients	Time (minutes)
1.	Mastication of NR	5
2.	ZnO	1
3.	Stearic Acid	1
4.	MBTS	1
5.	Sulfur	1
6.	Mixing for homogenization	2

2.3. Vulcanization Characteristics Testing

The vulcanization characteristics of the rubber compounds are identified based on the standard ASTM D5289-12 method at 150 °C using an Alfa 2000 moving die rheometer (Alfa Technologies, Akron, USA). In this test, the data on the curing characteristics of the rubber compounds are obtained, including the maximum and minimum torque, the difference between the maximum and minimum torque, optimum cure time (t_{90}), and scorch time (ts_2). The optimum cure time value is then used for molding the rubber compounds to be the test sample vulcanizate. The molding process is carried out on a KMC brand hydraulic press made in Japan.

2.4. Crosslink Density Test

The degree of an unfilled natural rubber vulcanizate is determined using the Mooney-Rivlin method [22, 23], which is based on the stress-strain behavior of the rubber with the following equation:

$$F = 2A_o\,(\lambda - \lambda^{-2})(C_1 + C_2/\lambda) \quad (1)$$

$$F / [2A_o\,(\lambda - \lambda^{-2})] = C_1 + C_2/\lambda \quad (2)$$

$$n_{phys} = C_1/RT \quad (3)$$

The intercept value of C_1 can be obtained by plotting the relationship curve of $F/[2A_o(\lambda - \lambda^{-2})]$ vs. $1/\lambda$. Furthermore, the value of C_1 can be used to determine the crosslink density of rubber vulcanizate according to equation (3).

2.5. Mechanical and Elastic Properties Test

The rubber vulcanizate is tested for its mechanical properties, such as Shore A hardness test according to ISO 48 standard, tensile strength, elongation at break test according to ISO 37 standard method, and tear resistance test based on ISO 34 standard. Then, rubber vulcanizate's elastic properties are examined through the LUPKE rebound resilience test according to the ASTM D1054 standard. A fixed compression test is also based on the ISO 815 type A standard.

2.6. Dynamic Shear Properties Testing

The rubber's dynamic shear properties are examined based on the ISO 4664-1 standard method using a four-block lap shear-type shown in Fig. 1a at 10 Hz, 100% strain for four test cycles.

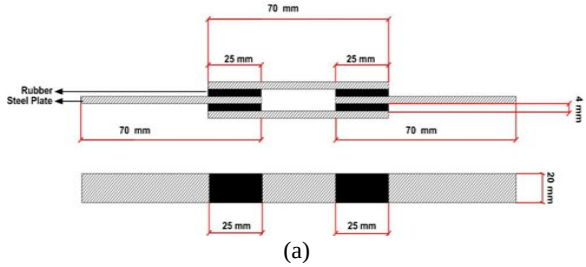
The results show a displacement (mm) vs. shear force (N) relationship curve in the form of a loop. The data are then analyzed using equations (4), (5), and (6) to obtain shear stiffness (K_H), damping ratio (h_{eq}), and effective shear modulus (G_{eff}) [4].

$$K_H = \frac{Q_1 - Q_2}{X_1 - X_2} \quad (4)$$

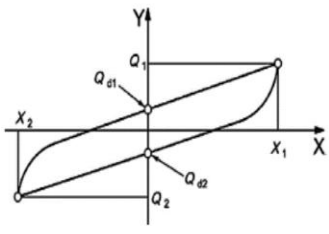
$$h_{eq} = \frac{2\,\Delta W}{\pi K_h\,(X_1 - X_2)^2} \quad (5)$$

$$G = \frac{K_H\ t_r}{A_r} \quad (6)$$

where K_H is the shear stiffness, h_{eq} is the equivalent damping ratio, Q_1 is the maximum shear force, Q_2 is the minimum shear force, X_1 is the maximum extension, X_2 is the minimum extension in the third cycle, ΔW is the area enclosed by the third hysteresis loop, and A_r and t_r are the one-layer rubber area and thickness.



(a)



(b)

Fig. 1 Dynamic shear test, (a) four-block lap shear-type specimen, (b) typical shear hysteresis loop

3. Results and Discussion

3.1. Curing Characteristics of Rubber Compounds

The determined curing characteristics of unfilled natural rubber compounds are the maximum torque (M_H), the minimum torque (M_L), the difference between the maximum and minimum torque, optimum cure time (t_{90}), and scorch time (ts_2). Based on the test results in Table 3, the curing characteristics of the rubber compound are strongly influenced by the sulfur ratio to the MBTS accelerator. The value of the sulfur ratio to the accelerator is closely connected to the types of sulfur vulcanization systems. Based on the sulfur ratio to the accelerator, unfilled natural rubber compounds with sample codes of A1, A2, and A3 are classified as efficient sulfur vulcanization systems. At the same time, A4 and A5 are respectively included as semi-efficient and conventional sulfur vulcanization systems. Increasing the sulfur ratio to the MBTS causes increasing maximum torque (M_H) and the difference between the maximum and minimum torque (M_H-M_L). It also triggers faster optimum cure time (tc_{90}) and scorches time (ts_2). The maximum torque (M_H) represents the maximum crosslinks established during the vulcanization [15]. The minimum torque (M_L) shows the compound's viscosity and also provides information regarding the compounds' processability [23]. Table 3 shows that the minimum torque values of all unfilled natural rubber compounds are relatively the same. The difference between maximum and minimum torsion (M_H-M_L) or torque delta is not directly connected to the total crosslink density of a rubber compound [15]. Table 3 shows that the torque delta increases when the sulfur ratio to the MBTS also increases. Therefore, the torque delta of unfilled natural rubber compounds using a conventional sulfur vulcanization system will be higher than NR compounds with semi-efficient and efficient sulfur vulcanization systems.

Table 3 Curing characteristics of unfilled NR compound

Curing Characteristics	Sulfur Ratio to Accelerator (S/MBTS)				
	(0.14)	(0.17)	(0.22)	(1.11)	(2.15)
M_H, dNm	2.93	3.19	3.55	5.75	7.01
M_L, dNm	0.36	0.39	0.49	0.75	0.41
$M_H - M_L$, dNm	2.57	2.8	3.06	5.00	6.60
ts_2, min:sec	25:38	26:11	23:56	14:46	9:56
tc_{90}, min:sec	30:42	20:15	17:33	9:36	5:07

3.2. Crosslink Density

In this research, the crosslink density of unfilled natural rubber vulcanizate was set using the Mooney-Rivlin method, and the crosslink density values are shown in Table 4. The crosslink density values were related to the sulfur amount that reacts with the molecular rubber chains through the crosslink. A higher amount of sulfur triggers improved formation of crosslinks. Sansanee Srichan and Sarawut Prasertsri [20] stated that the types of sulfide crosslinks formed in the vulcanization process include monosulfide, disulfide, or polysulfide crosslinks which are influenced by the sulfur vulcanization system, vulcanization time, and temperature. Table 4 shows that the increasing sulfur ratio to MBTS will also increase the crosslink density values of a rubber vulcanizate. Therefore, the sulfur ratio to the accelerator can determine whether the sulfur vulcanization system is conventional, semi-efficient, or efficient. The unfilled rubber vulcanizate using a conventional sulfur vulcanization system produces higher crosslink density values than the NR vulcanization using semi-efficient and efficient systems. These crosslink density values can affect a natural rubber vulcanizate's mechanical, viscoelastic, and vibration damping properties.

Table 4 Crosslink density values on unfilled NR vulcanizate

Sample Code	Sulfur/MBTS	Crosslink Density by Mooney-Rivlin Method (mol/cm^3)
A1	0.14	7.45×10^{-6}
A2	0.17	2.38×10^{-5}
A3	0.22	2.85×10^{-5}
A4	1.11	5.20×10^{-5}
A5	2.15	7.16×10^{-5}

3.3. Mechanical and Elastic Properties

The mechanical properties of natural rubber vulcanizate were strongly influenced by the density and type of crosslinks [13, 14, 17, 19, 21]. The mechanical properties of natural rubber vulcanizate obtained from varying sulfur ratios to the MBTS accelerator are presented in Fig. 2. This research examined mechanical properties, including hardness, tear strength, tensile strength, and elongation at break.

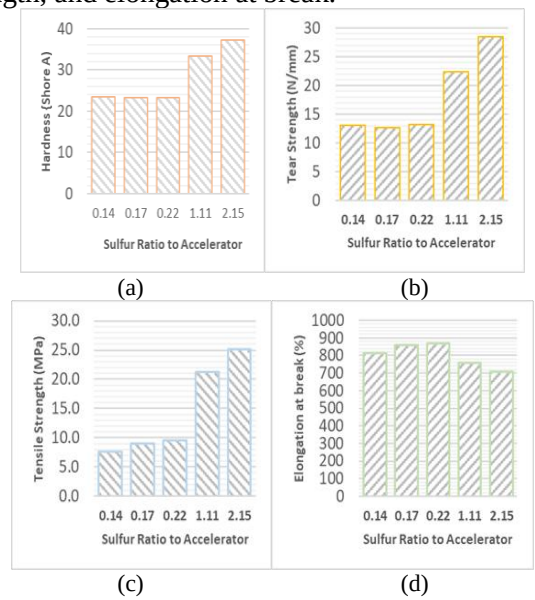


Fig. 2 The relationship of variations in the sulfur ratio to accelerator to the mechanical properties of unfilled NR vulcanizate: (a) hardness, (b) tear strength, (c) tensile strength; (d) break elongation

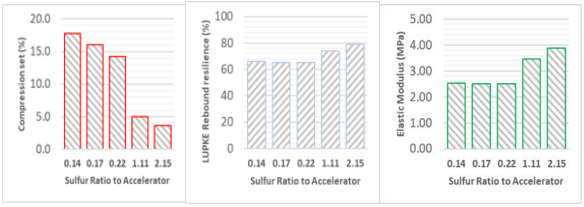
Fig. 2 shows that increasing sulfur ratio of sulfur to

the accelerator (MBTS) caused an increase in the hardness, tear strength, and tensile strength level and also caused decreasing elongation at break properties of an unfilled rubber vulcanizate. In addition, the increasing sulfur ratio to accelerator caused higher crosslink density values and further increased the strength and elastic properties [19]. Based on the results shown in Fig. 2, the increase in the sulfur ratio to the accelerator also increases the material strength, indicated by the increasing tear and tensile strength. Furthermore, this event is associated with increased crystallinity upon stretching [26, 27]. Furthermore, from Fig. 3, it can be seen that an increase in the sulfur ratio to the accelerator caused an increase in the elastic properties, as indicated by a lower compression set (Fig. 3a), higher LUPKE rebound resilience value (Fig. 3b), and higher elastic modulus values (Fig. 3c).

The elastic modulus value in Fig. 3c is obtained based on the indentation technique through the relationship of the Shore A hardness value to the elastic modulus according to the following equation proposed by Kunz and Studer [28]:

$$E_H = \left(\frac{1-v^2}{2r_d}\right) x \left(\frac{0.549 + (0.07516\ x\ Sh_A)}{0.025\ x\ (100 - Sh_A)}\right) x \left(2.6 - (0.02\ x\ Sh_A)\right) \quad (7)$$

Sh_A means the Shore-A hardness value, r_d is the tip radius of the durometer (0.395 mm), and v is the assumed value of the Poisson ratio of 0.475.



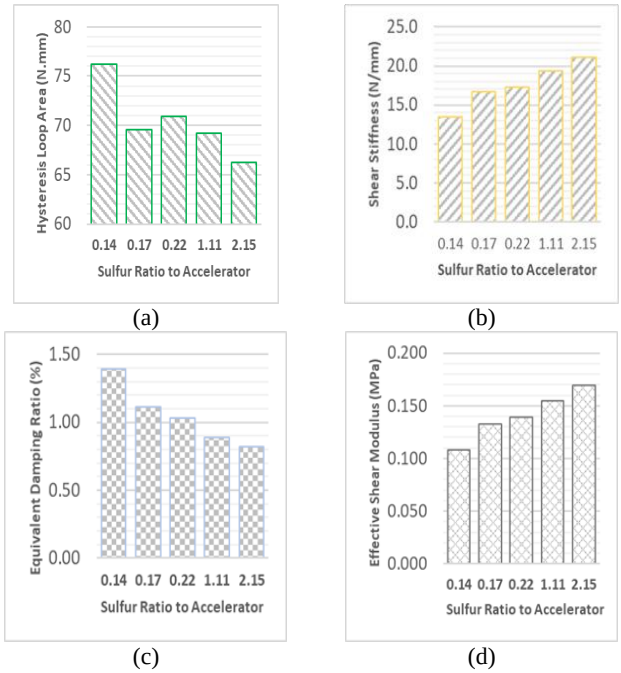
(a) (b) (c)

Fig. 3 The relationship of variations in the sulfur ratio to accelerator on the elastic properties of unfilled natural rubber vulcanizate: (a) compression set, (b) LUPKE rebound resilience, (c) elastic modulus

3.4. Viscoelastic Properties and Vibration Damping

Rubber belongs to viscoelastic materials with specific viscous and elastic properties. The viscoelastic behavior of natural rubber vulcanizate can be identified by testing its dynamic properties but depends on the strain frequency, strain amplitude, and temperature [5]. Hysteresis values can demonstrate viscoelastic properties by measuring dynamic properties [4, 8]. The hysteresis event shows the energy lost per cycle during rubber deformation related to the vibration damping capacity [8].

In the rubber compounds vulcanizate, the hysteresis value is greatly affected by the types of raw rubber and its chemicals [8]. The influential chemicals include the types and amount of the filler [8], type and number of vulcanizing materials [15], softener [8], and resin materials [9]. Based on the dynamic shear properties test results shown in Fig. 4, it can be seen that the values of the hysteresis loop area, shear stiffness, equivalent damping ratio, and effective shear modulus are affected by the sulfur ratio to the accelerator in natural rubber vulcanizate. Fig. 4a shows that the dynamic shear properties test resulted in various hysteresis loop areas, significantly influenced by the sulfur ratio to MBTS accelerator. The hysteresis loop area value means that natural rubber vulcanizate is viscoelastic. The highest hysteresis loop area value and equivalent damping ratio occur in natural rubber vulcanizate, with sulfur to accelerator ratio of 0.14. Increasing the sulfur ratio to the accelerator in the unfilled rubber vulcanizate caused an increase in the shear stiffness (Fig. 4b) and effective shear modulus (Fig. 4d) values. However, the equivalent damping ratio will decrease (Fig. 4c). The sulfur ratio to MBTS accelerator can affect the crosslink density so that this ratio increase can cause the vulcanizate to become stiffer, indicated by higher hardness values (Fig. 2a). It means that the shear stiffness values may increase due to increasing values of the NR vulcanizate hardness. The shear stiffness values greatly influence the equivalent damping ratio and the effective shear modulus. The higher shear stiffness values result in a decrease in the equivalent damping ratio and an increase in the effective shear modulus values.



(a) (b) (c) (d)

Fig. 4 The relationship of the sulfur ratio to accelerator to the dynamic shear properties of unfilled natural rubber vulcanizate: (a) hysteresis loop area, (b) shear stiffness, (c) damping ratio, and (d) effective shear modulus

4. Conclusion

4.1. Scope of the Results

The compounds curing characteristics, crosslink density, and mechanical, elastic, viscoelastic, and vibration dampening properties of unfilled natural rubber vulcanizate are strongly influenced by the sulfur ratio to accelerator used. Testing results showed that

the increment of sulfur to MBTS accelerator ratio increased crosslink density value. The highest crosslink density was measured at a 7.16 x 10^{-5} mol/cm^3 obtained by NR vulcanizates containing sulfur to MBTS accelerator ratio at 2.15. This ratio also produced optimum value for mechanical properties (tear and tensile strength), elastic properties (compression set, LUPKE rebound resilience, and elastic modulus), and the highest effective shear modulus value. The value of tear strength, tensile strength, compression set, LUPKE rebound resilience, elastic modulus, and an effective shear modulus were 28.5 N/mm; 25.2 MPa; 3.65%; 79; 3.89 MPa, dan 0.169 MPa. In addition, the optimum value of vibration dumping was obtained at 1.39% of an equivalent damping ratio produced by NR vulcanizates containing sulfur to MBTS accelerator ratio at 0.14.

4.2. Novelty, Limitation, and the Research Perspectives

The natural rubber has good elasticity properties and low vibration damping capacity. Therefore, modification of the properties through crosslink in natural rubber vulcanizates molecular chains is required to produce a better vibration isolator. In addition, the sulfur ratio of the accelerator added to natural rubber compounds can control the crosslink density in the rubber molecules and influence the rubber vulcanizate's mechanical properties, especially viscoelasticity properties and strength. These variables are essential to developing NR vulcanizates properties appropriate to the vibration isolator product requirement.

Dynamic Mechanical Analysis (DMA) is usually utilized to investigate the vibration damping capacity of a rubber vulcanizate. The dynamic shear properties testing determined the vibration damping capacity in this research. A study on the correlation between crosslink density and dynamic shear properties of NR vulcanizates has not been conducted. The correlation between crosslink density and dynamic shear properties of NR vulcanizates, including hysteresis loop area, shear stiffness, equivalent damping ratio, and effective shear modulus, is revealed in this report. Crosslink density is determined by the Mooney-Rivlin method based on the stress-strain behavior of the rubber and correlated to the dynamic shear properties. The compound formulation technique could set the crosslink density of the natural rubber compounds to achieve the optimum value of the viscoelasticity and damping properties of NR vulcanizates.

The crosslink density of NR vulcanizates represents as total crosslink density. This research was to study the effects of total crosslink density on the NR vulcanizates' properties. In contrast, the composition of types of crosslink density such as monosulfide, disulfide, and polysulfide crosslink density was ignored. For further study, the correlation between types of crosslink density and dynamic shear properties will be reported separately. Based on the influence of sulfur ratio to accelerator on the crosslink density of NR vulcanizates, the research focused on increasing the vibration damping capacity of rubber vulcanizates and designing a rubber compound formulation for the preparation of a specific rubber isolator or rubber product.

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