| 1  | Type of Article (Original Article)   |  |  |  |  |  |
|----|--|--|--|--|--|--|
| 2  | THE EFFECT OF SULFUR RATIO TO 2-2'-DITHIOBENZOTHIAZOLE   |  |  |  |  |  |
| 3  | ACCELERATOR ON VISCOELASTIC, VIBRATION DAMPING, AND  |  |  |  |  |  |
| 4  | THERMAL STABILITY PROPERTIES OF GUM NATURAL RUBBER   |  |  |  |  |  |
| 5  | VULCANIZATES   |  |  |  |  |  |
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| 14 |  |  |  |  |  |  |
| 15 | Abstract   |  |  |  |  |  |
| 16 | It is well-recognized that the sulfur to accelerator (S/A) ratio has greater                                       |  |  |  |  |  |
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atly influenced the nature of rubber vulcanizates. Viscoelasticity, vibration damping, and 17 thermal stability are important properties of rubber vulcanizates as material for vibration 18 isolators. This research aims to study the ratio effects that fall anywhere between sulfur 19 to 2-2'-dithiobenzothiazole (MBTS) accelerator on viscoelastic, vibration damping, and 20 21 thermal stability conditions of gum natural rubber (NR) vulcanizates. The study of the 22 viscoelastic and vibration damping properties was determined by a rubber process analyzer (RPA), while the thermal stability was investigated by thermogravimetric 23 analysis (TGA). The results showed that the gum NR vulcanizates that possess the 24

sulphur to MBTS accelerator ratio at 1.11 had the best viscoelastic and vibration
damping properties as a rubber isolator. However, in terms of thermal stability
properties, the gum NR vulcanizates that possess the sulfur to MBTS accelerator ratio at
2.15 was excellent, among others.

29 Keywords: rubber; sulfur, viscoelastic, vibration damping, thermal stability

30 1. Introduction

Natural rubber (NR) is an Indonesian prominent plantation commodity, but it is not yet popular to use and still has no high added value. Therefore, there should be further studies on the diversification and development of NR products to increase their values and domestic consumption rate. Rubber products are potential for many usages, such as vibration isolators or dampers for seismic protection of buildings and flyover structures, machinery, automotive, and shipboards (Polukoshko, Martinovs, & Zaicevs, 2018).

Vibration isolators or dampers can be found in automotive fields. The rubber 38 product demands align with the development of the automotive market. The products 39 40 are developed based on material engineering to obtain optimum viscoelasticity, vibration dampening, and thermal stability properties according to material 41 42 requirements. Good material for vibration isolator are indicated by high values of 43 damping factor, viscous modulus, thermal stability, and low values of elastic shear modulus (Pochivalov et al., 2020; Zhou, Yu, Shao, Zhang, & Wang, 2016). NR has 44 lower vibration damping properties than synthetic rubber, known as the smallest tangent 45 delta value or loss factor (Halladay & Jaglowski, 2017). Good damping materials for 46 outdor and machinery applications should exhibit a high loss factor or tangent delta 47  $(\tan \delta \ge 0.3)$  over a wide temperature range (Xiaozhen He, Ming Qu, & Xinyan Shi, 48

2016). The low vibration damping properties are caused by its viscoelastic properties
having more elastic components than the viscous ones in its molecular chain structure.
Therefore, it's necessary to conduct a study to increase the vibration damping property
of NR.

The viscoelastic properties of rubber material can be determined using the 53 dynamic properties test, such as dynamic mechanical analysis (DMA) or rubber process 54 analyzer (RPA). The results depend on the frequency and amplitude of the strains and 55 56 also the temperature (Hentschke, 2017). The most important property that determines the vibration damping is the hysteresis value. The hysteresis value is obtained from the 57 tangent delta measurement. The types of raw rubber and rubber chemicals (Halladay & 58 59 Jaglowski, 2017) are the influencers of the rubber vulcanizates' hysteresis value, and the most influential chemicals are the types and amounts of filler materials (Halladay & 60 Jaglowski, 2017), vulcanizing materials (Le Cam, 2017; Shi et al., 2019), softeners or 61 plasticizers (Halladay & Jaglowski, 2017) and resinous materials (Su, Zhao, Xu, & 62 Zhang, 2015). 63

64 Polymeric viscoelastic properties are generally influenced by the molecular chain structure (Karl, Kirsch, Faderl, Perko, & Fras, 2020; Vašina, Pöschl, & Zádrapa, 65 2018) and main composition (Karl, Kirsch, Faderl, Perko, & Fras, 2020; Tolpekina, 66 Pyckhout-Hintzen, & Persson, 2019; Vašina, Pöschl, & Zádrapa, 2018). The rubber's 67 molecular chain structure can be modified to change its vibration damping and 68 viscoelastic properties (Halladay & Jaglowski, 2017; Lei, Zhang, Kuang, & Yang. 69 70 2019; Vašina, Pöschl, & Zádrapa, 2018;). The engineering technique of molecular structure includes certain treatments that can change the number and type of sulfide 71 crosslinks formed in the rubber molecular chain. The number and types of crosslinks 72

73 between sulfides inside the rubber vulcanizates' materials, properties and more are strongly affected by the ratio of sulfur to its accelerators (Larpkasemsuk, Raksaksri, 74 75 Chuayjuljit, Chaiwutthinan, & Boonmahitthisud, 2019), while the sulfide crosslinks density greatly affects the properties of the rubber vulcanizates (Alshabatat & Abouel-76 Kasem, 2021; Han et al., 2020; Kim, Park, Lee, & Seo, 2020; Shi et al., 2019). Some 77 researchers have studied and observed the vibration damping properties of NR or 78 synthesis. The studies consist of some treatments that change the viscoelastic properties, 79 80 such as how the type and amount of filler affect the properties, the effect of softening agents, the sulfur vulcanization system, the effect of rubber blend, or the addition of 81 resin (Halladay & Jaglowski, 2017; Koupai, Bakhshi, & Tabrizi, 2017; Lei, Zhang, 82 83 Kuang, & Yang. 2019; Li et al., 2019; Ma, Zhang, Liu, & Wu, 2019; Mohamad et al., 2017; Murniati et al., 2020; Wang et al., 2017; Wang et al., 2018). Hence, the 84 molecular chain structure of NR changing the number and type of sulfide crosslinks can 85 affect its viscoelastic and vibration damping properties. 86

This research studies the characteristics of the viscoelastic properties, vibration damping, and thermal stability of gum NR vulcanizates. The influence of the ratio of sulfur to MBT accelerator on viscoelastic, damping, and thermal stability properties of gum NR vulcanization is explored in more detail to identify a natural rubber compound design that fits with the requirements as vibration isolators or dampers for automotive applications (durability against thermal degradation).

93 2. Materials and Methods

94 **2.1 Materials** 

Rubber compound was made by mixing NR subtype SIR 20 (TSR 20) as a raw
elastomer with rubber chemicals. Furthermore, the rubber chemicals was used consist of

97 the following materials:: 1) Zinc oxide (ZnO) UN 3077 from Lanxess, Germany 98 (activating agents), 2) Aflux®52 from Lanxess Germany (stearic acid), 3) 2-2'-99 dithiobenzothiazole (MBTS) from Kemai, China (accelerator), and 4) Midas SP 325 100 sulphur from Miwon Co., Japan (vulcanizing materials). The entire chemicals for rubber 101 compounds have been tested and have passed the technical quality level. The rubber 102 compound formula is for different sulfur doses, based on the MBTS accelerator that is 103 related to the sulfur, and the formula is displayed in Table 1.

104 Tetrahydrofuran (THF) and *n*-hexane were used for sample purification, then 105 toluene was used for sample swelling. The solvent were all obtained from Sigma-106 Aldrich. For determination of the crosslink density and distribution, 2-propanethiol 107 ( $\geq$ 98%), hexanethiol ( $\geq$ 95%), and hexylamine ( $\geq$ 98%) were all provided by Sigma-108 Aldrich.

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#### 109 2.2 The Production of Rubber Compound

The rubber compound was produced using a mixture of rubber and chemicals in 110 a laboratory-scale open rubber mixing roll mill. It has a 1000 gram/batch capacity using 111 112 a German-made brand, Berstorff. The ASTM 3182 standard is the base of the rubber mix production, where the procedures are shown in Table 2. In the mastication process, 113 natural rubber was reduced in viscosity to make it easier to mix rubber with chemicals. 114 115 The already-masticated rubber will be smoother, known by the level of plasticity. Then, the rubber mix chemicals are mixed with the rubber. The first chemical is ZnO (zinc 116 oxide), stearic acid, the accelerator, and finally, the vulcanizing sulfur. The next step 117 118 after the addition of the chemical ingredients is milling processes the natural rubber.

The value of the sulfur to accelerator ratio lower than 0.3 is an efficient type of
 sulfur vulcanization system. Next, rubber vulcanization included as the semi-efficient

type of sulfur vulcanization has a ratio value between 0.4 to 2. Meanwhile, the rubber
vulcanization with a conventional sulfur vulcanization system has a higher ratio than 2
(Bellander, 1998). Based on the criteria for grouping the type of sulfur vulcanization
system, the NR vulcanization with a sulfur ratio to MBTS accelerator of 0.14 and 0.22
is efficient sulfur vulcanization, and the ratios of 1.11 and 2.0 are semi-efficient and

126 conventional.

127 **2.3 Determining the Curing Characteristics** 

128 The ASTM D5289-12 standard at 150°C with an Alpha Moving Die Rheometer (MDR) 2000 (Alfa Technologies, Akron, USA) is the standard method used for 129 characterizing the rubber compounds' vulcanization. Eventually, the characterization 130 131 standard leads the experiment to determine the rubber compounds' curing characteristics using databases from the maximum and minimum torque modulus, the 132 delta torque, the optimum curing time  $(t_{90})$ , and the scorch time  $(ts_2)$ . Next, the 133 experiment sets the optimum cure time value for molding the rubber compounds as the 134 test sample vulcanizate. The experiment conducts the molding process with a Japan-135 136 made hydraulic press (KMC).

#### 137 **2.4 Determination of the Crosslink Density and Distribution**

In this research, crosslink density was determined by swelling measurement. Before determining the crosslink density of rubber vulcanisates, organic additives and impurities were first removed by THF and *n*-hexane. The rubber vulcanisates (10 mm x 10 mm x 1 mm) were immersed in *n*-hexane for 3 days and THF for 2 days, then dried for 2 days at room temperature. Determination of the crosslink density was conducted on the dried rubber vulcanizates by swelling in toluene for 3 days. The weights of the swollen vulcanizates were then measured. The proportion of each crosslink type was

156 Flory-Rehner equation (1).

$$v = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{2V_1(V_r^{1/3} - V_r/2)}$$
(1)

- where  $V_r$  is the volume fraction of the crosslinked polymer,  $\chi$  is the interaction parameter between the polymer and solvent,  $V_1$  is the molar volume of the swelling
- 159 solvent (i.e, 106.27 cm<sup>3</sup>/mol for toluene). The  $V_r$  is determined by equation (2)

$$V_{r} = \frac{\frac{(W_{o} - W_{f})}{\rho_{r}}}{\frac{(W_{o} - W_{f})}{\rho_{r}} - \frac{(W_{o} - W_{a})}{\rho_{s}}}$$
(2)

160 Where  $W_{o}$  (g) is the weight of the rubber sample before swelling,  $W_{f}$  (g) is the weight of 161 the filler,  $W_{a}$  (g) is the weight of the rubber sample after swelling,  $\rho_{r}$  (g/cm<sup>3</sup>) is the

162 density of rubber, and  $\rho_s$  (g/cm<sup>3</sup>) is the density of solvent.

#### 163 **2.5 Testing the Dynamic and Vibration Damping Properties**

The dynamic properties and vibration damping of gum NR compound with 164 165 variations in the ratio of sulfur to MBTS accelerator are examined using a Rubber Process Analyzer (RPA 2000 Elite, TA Instrument). It is based on Gao, Xie, Zhang, 166 Gui, & Huang (2015). The measurement was conducted in the uncured state using an 167 RPA 2000. The uncured samples were reduced to 6 grams and placed into a mold 168 chamber. The specification of uncured samples as gum NR compound compositions is 169 shown in Table 1. The sample was then subjected to a frequency sweep from 0.08 - 50 170 Hz in a single sweep at a constant strain amplitude of 0,5° and 90°C of temperature. 171 2.6 Thermal Properties Testing 172

The vulcanizate samples of gum NR compound with various ratios of sulfur to MBTS accelerator are identified using TGA based on Yunus *et al.* (2019). The TGA test is conducted on vulcanized samples of NR compound (9-10 mg) using an aluminium (Al) crucible under a nitrogen atmosphere. The tested temperature range is around 0–550°C, using heating mode and 10°C/minute rate.

#### 178 **3. Results and Discussion**

#### 179 **3.1 Curing Characteristics of Rubber Compound**

The maximum torque modulus  $(M_H)$  and minimum torque modulus  $(M_L)$ , as well as the difference between  $M_H$  and  $M_L$  (or the delta torque), the optimum curing time (t<sub>90</sub>), and scorch time (ts<sub>2</sub>), are the curing characteristics of rubber mixes. They were determined by a rheometer and used to obtain the data on the finished rubber product processing. According to the test results in Figure 1, the curing characteristics of the gum NR compound (maximum torque modulus, minimum torque modulus, the delta torque, the optimum curing time, and the scorch time) were greatly affected by the 187 ratio of sulfur to the MBTS accelerator. This ratio is connected to the type of sulfur vulcanization system formed in rubber vulcanizates. It seems that the gum NR 188 189 compound with sample codes A1(0.14), and A2(0.22) belongs to the efficient type of sulfur vulcanization system. Meanwhile, the sample codes of A3(1.11) and A4(2.15) are 190 categorized as semi-efficient and conventional in the sulfur vulcanization systems. The 191 192 improving ratio value of sulfur to the MBTS accelerator will increase the maximum value of torque  $(M_H)$  and the delta torque  $(M_H-M_L)$  values. It can also enforce optimum 193 194 cure  $(t_{90})$  and scorch  $(ts_2)$  times. The maximum torque value  $(M_H)$  of the rubber compound indicates the maximum value of allowed crosslinks to form during the 195 vulcanization process (Shi et al., 2019), while the minimum torque value (ML) implies 196 197 the mixtures' viscosity indicator and other information related to the rubber compound's processability (Hiranobe *et al.*, 2021). Figure 1(a) shows that the maximum torque value 198 199 will increase if the ratio of sulfur to MBTS accelerator increases. The minimum torque value of all treatments for gum NR compounds (Figure 1(b)) is relatively the same (0.3 200 to 0.8 dNm). Figure 1(a) also proves that the maximum number of crosslinks increases 201 202 if the number of the sulphur ratio to accelerator also increases. It is correlated with an 203 increased maximum torque value.

Another curing characteristic of rubber compounds is delta torque ( $M_{H}-M_{L}$ ). It is indirectly related to the total crosslink density (Shi *et al.*, 2019). The sulfur in rubber technology acts as a crosslinking material in the molecular chain structure. A higher amount of sulfur added to the natural rubber compound will also increase the amount of crosslinks. As we see in Figure 1(c), the delta torque increases when the comparison between the amount of sulfur to the accelerator also improves. The gum NR compound's delta torque, which uses a conventional sulfur vulcanization system, tends to have higher values than the ones using semi-efficient and efficient sulfurvulcanization systems.

Figures 1(d) and 1(e) conclude that increasing the ratio of sulfur to MBTS accelerator can maximize optimum cure time (t<sub>90</sub>) and push scorch time (t<sub>s2</sub>) at the specified vulcanization temperature. The increasing amount of sulfur added to the rubber compound can speed up and save the reaction time of crosslink formation in the rubber-molecular chain.

#### 218 **3.2 Crosslink characteristics of NR vulcanizates**

Results for total crosslink density and distribution of crosslink density are summarized in Table 3. The total, disulfide, and polysulfide crosslink density were greatly affected by the ratio of sulfur to the MBTS accelerator. From these results, it can be shown that monosulfide cross-links were not observed. It concluded that the NR vulcanization system with sulfur and MBTS was not formed the monosulfide crosslinks. For the MBTS accelerator cure system, after immersion in the chemical probe

solution for polysulfide and disulfide cleavage, NR vulcanizate was dissolved.

226 The improving ratio value of sulfur to the MBTS accelerator will increase the total crosslink density and polysulfide crosslink density value. Whereas the disulfide 227 crosslink density value was observed to increase up to the sulfur ratio to MBTS 228 accelerator at 1.11 and after that, it was observed to decrease. The sulfur in rubber 229 vulcanization acts as a crosslinking agent in the molecular chain structure. A higher 230 amount of sulfur added to the natural rubber compound will also increase the total 231 232 crosslink density, but the increase was not proportional to the total crosslink density and distribution of crosslink density. Boonkerd et al. (2016) stated that the percentage of 233

## 234 polysulfide crosslink density was not proportional with increasing the sulfur ratio to 235 accelerator.

#### 236 **3.3 Characteristics of Viscoelastic and Vibration Damping Properties**

We consider natural rubber a viscoelastic material and a combination of viscous 237 and elastic properties. The rubber's viscoelastic behavior can be acknowledged through 238 239 testing the properties that can change. It also depends on the frequency and amplitude of the strains and also the temperature (Hentschke, 2017). The viscoelastic properties can 240 241 be seen using hysteresis values through the dynamic properties' measurements (Halladay & Jaglowski, 2017; Koupai, Bakhshi, & Tabrizi, 2017). Hysteresis is the 242 amount of energy spent during rubber deformation, which we determine as per cycle. 243 244 Later, the hysteresis values determine the dissipating abilities during vibrations of the rubber material (Halladay & Jaglowski, 2017). Tangent delta or loss factor measures the 245 hysteresis phenomenon to show the energy dissipation capacity of a viscoelastic 246 material subjected to reciprocating motion. This energy dissipation affects the 247 mechanical vibration damping capacity. A higher tangent delta value means higher 248 249 vibration damping capacity. The tangent delta value can be obtained from the ratio 250 between viscous and elastic shear modulus.

Rubber Process Analyzer (RPA) is a testing tool that functions like a straincontrolled rotational shear rheometer. The dynamic properties of gum NR compounds are examined with different ratios of sulfur to MBTS accelerator. The properties were determined using the RPA. The dynamic properties can be seen from the curve profile of the relationship among elastic shear modulus, viscous modulus, and complex shear modulus with frequency. The vibration damping properties of gum NR compounds were shown from the tangent delta relationship curve profile with the frequency. Based 258 on the dynamic properties test, using RPA at a temperature of 90°C (as shown in Figure 259 2), the gum NR compound with different ratios of sulfur to MBTS accelerator has the 260 same curve profile of the dynamic properties' relationship with frequency (elastic shear 261 modulus, viscous modulus, and complex shear modulus). The gum NR compound with 262 a sulfur vulcanization system that is semi-efficient (code A3(1.11)) shows a drastic 263 change in the elastic absolute value of the curve profile (Figure 2(a)) and complex shear modulus (Figure 2(c)) towards lower values starting at a frequency of 3.3 Hz. There is 264 265 also a shift in the viscous modulus curve profile (Figure 2(b)) towards higher values starting at a frequency of 25 Hz. An gum NR compound with the efficient (A1(0.14) 266 and A2(0.22)) and conventional (A4(2.15)) type sulfur vulcanization systems have a 267 268 relatively small shift in the value of the dynamic properties curve profile.

Figure 2(d) shows the vibration damping properties of the gum NR compound at 269 270 different ratios of sulfur to MBTS accelerator in the tangent delta-frequency relationship The gum NR compound using a semi-efficient sulfur vulcanization 271 curve profile. system (code A3(1.11)) generates a significant shift in the tangent delta curve profile 272 273 towards higher values starting at a frequency of 4.6 Hz. The gum NR compound with the efficient (A1(0.14)) and A2(0.22) and conventional (A4(2.15)) sulfur vulcanization 274 275 systems have a relatively small shift in the value from the resulting tangent delta curve 276 profile. The correlation curve of the tangent delta to the frequency from the RPA test indicates gum NR compound with a semi-efficient sulfur vulcanization system has 277 better vibration damping properties than an efficient and conventional type 278 279 vulcanization system. It means that the gum NR compound using a semi-efficient sulfur vulcanization system can produce rubber vulcanizate with a component of more viscous 280 properties than the component of elastic properties in the rubber's molecular structure. 281

282 According to the results in Table 3 and Figure 2(d), It was found a correlation between the distribution of crosslink density and vibration-damping properties of rubber 283 284 vulcanizates. Sombatsompop (1998) stated that the viscoelastic properties were affected by the crosslink types present in NR compounds and Nie et al. (2021) stated that 285 polysulfide crosslink type is attributed to the flexibility of rubber vulcanizates. The gum 286 NR compound using a semi-efficient sulfur vulcanization system (code A3(1.11)) have 287 higher value of disulfide crosslink density (Table 3) and the tangent delta (Figure 2(d)) 288 than an efficient and conventional type vulcanization system. The disulfide crosslink 289 type and density is predicted to give a greater contribution to the viscous properties than 290 the elastic properties in the rubber's molecular structure. Whereas the type and density 291 292 of polysulfide cross-links is predicted to give a greater contribution to the elastic properties. 293 If carbon black is further filled in NR compound, the viscoelastic properties will 294 be affected. According to Poschl et al. (2020), the damping characteristics of 295 mechanical vibration are influenced by the carbon black type and its amount. The 296 297 stiffness and hardness of rubber vulcanizates generally increased with an increase in the amount of carbon black filled in rubber vulcanizates. This is resulting in increased 298

299 elasticity and decrement in damping characteristics.

#### **300 3.4 Thermal Stability Properties**

In this study, thermogravimetry analysis (TGA) identifies the thermal stability or thermal degradation behavior of gum NR vulcanizates within different ratios of sulfur to MBTS accelerator. The thermal stability of the material is observed at varied ratios of sulfur to MBTS accelerator (0.14; 0.22; 1.11; and 2.15). The observed sulfur to accelerator ratios is correlated with the type of sulfur vulcanization system formed inrubber vulcanization.

307 Both Figure 3 and Table 4 show the computations, process and results from the TGA tests. Figure 3 indicates that the sulfur versus MBTS ratio affects the thermal 308 balances inside gum NR vulcanizates. Then, the experiment also notes the start and end 309 310 of the decomposition processes. Such things involve temperature tests between four samples, which we can witness in  $T_{\text{onset}}$  and  $T_{\text{end}}$  in Table 4. The gum NR vulcanizates 311 312 with the 2.15 value in the sulfur versus MBTS comparisons (conventional system) generate a higher degradation temperature of the material compared to the NR 313 vulcanizates with a ratio of sulfur to other accelerators set out in this research. It means 314 315 the thermal stability properties of gum NR with a conventional-type sulfur vulcanization system with a sulfur ratio to MBTS accelerator of 2.15 produces better thermal stability 316 properties than NR vulcanizates with an efficient system with a ratio of 0.14 and 0.22. 317 This finding is different from previous studies in that natural rubber vulcanizates with 318 an efficient sulfur vulcanization system have better thermal stability properties than 319 320 conventional or semi-efficient sulfur vulcanization systems (Hayeemasae & Masa, 2020; Larpkasemsuk, Raksaksri, Chuayjuljit, Chaiwutthinan, & Boonmahitthisud, 321 322 2019). The difference may be due to the different types of accelerators. Each accelerator 323 can produce a different number of crosslinked types (monosulfide, disulfide, and polysulfide crosslinks), even in the same amount of sulfur and accelerators (Boonkerd, 324 325 Deeprasertkul, & Boonsomwong, 2016).

Broken bonds influence the thermal degradation of natural rubber vulcanization among atoms, including the number and type of crosslinks in rubber vulcanizates (monosulfide, disulfide, and polysulfide crosslinks). The polysulfide bond has a strength 329 of less than 262 kJ/mol, while the monosulfide bond is 280 kJ/mol (Hayeemasae & 330 Masa, 2020). In the system that vulcanizes the sulfur, the sulfur to accelerator (S/A) 331 ratio can influence the number of types of crosslinks formed. More numbers and types of monosulfide can generate better thermal stability properties. The monosulfide, 332 disulfide, and polysulfide crosslinks will affect thermal stability. The thermogram curve 333 334 presented in Figure 3(b) show gum NR vulcanizates' temperatures with conventional (regular) systems of sulfur vulcanization tend to be heat stable more than others in this 335 336 experiment. The initial degradation occurs at a temperature of 353°C. The final 337 degradation is at a temperature of 409.3°C.

#### **338 4. Conclusions**

339 The research findings conclude that:

The values of maximum torque value (M<sub>H</sub>), the difference between maximum versus
 minimum torque values (M<sub>H</sub>-M<sub>L</sub>), and the optimum curing time speed-ups (t<sub>90</sub>), as
 well as the scorch time (ts<sub>2</sub>), can be increased by increasing the ratio of the sulfur to
 the MBTS accelerators in gum NR compounds.

2. The viscoelastic properties (elastic shear modulus, viscous modulus, complex shear
modulus, and tangent delta) and thermal stability properties of gum NR compounds
were affected by the ratio of sulfur to MBTS accelerator.

347 3. The gum NR vulcanizates having a sulfur ratio with an MBTS accelerator of 1.11

- 348 generates better viscoelastic and vibration damping properties as a vibration damping
- 349 material for automotive purposes.

4. The gum NR vulcanizates containing a sulfur ratio with an MBTS accelerator of 2.15produces optimum thermal stability.

352 5. Using the semi-efficient type of sulfur vulcanization in gum rubber vulcanizates with
a S/A ratio value of 1.11 was preferable as vibration isolators for automotive
applications, but its thermal stability properties need to be increased.

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Type of Article (Original Article)

## THE EFFECT OF SULFUR RATIO TO 2-2'-DITHIOBENZOTHIAZOLE ACCELERATOR ON VISCOELASTIC, VIBRATION DAMPING, AND THERMAL STABILITY PROPERTIES OF GUM NATURAL RUBBER VULCANIZATES



(e)

Figure 1 Curing Characteristics of gum NR compound at different ratios of sulfur to the accelerator, (a) maximum torque, (b) minimum torque, (c) delta torque, (d) scorch time, and (e) optimum cure time



Figure 2 Dynamic properties curve for frequency variation of gum NR compound at different ratios of sulfur to the accelerator, (a) elastic shear modulus, (b) viscous modulus, (c) complex shear modulus, and (d) tangent delta



Figure 3 TGA curve of gum NR vulcanizates (a) in one sample, (b) in a combination of four samples with various ratios of sulfur to the accelerator

#### Type of Article (Original Article)

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| Table 1. Gum NR compound formula |                      |              |                          |                 |               |                        |
|----------------------------------|----------------------|--------------|--------------------------|-----------------|---------------|------------------------|
|                                  | Material Composition |              |                          |                 |               |                        |
| Sample code                      | TSR 20               | ZnO<br>(phr) | Stearic<br>Acid<br>(phr) | Sulfur<br>(phr) | MBTS<br>(phr) | Ratio<br>(Sulfur/MBTS) |
| A1(0.14)                         | 100                  | 5            | 2                        | 0.20            | 1.45          | 0.14                   |
| A2(0.22)                         | 100                  | 5            | 2                        | 0.30            | 1.35          | 0.22                   |
| A3(1.11)                         | 100                  | 5            | 2                        | 1.50            | 1.35          | 1.11                   |
| A4(2.15)                         | 100                  | 5            | 2                        | 2.90            | 1.35          | 2.15                   |

Note: The phr letter means parts per hundred rubber (phr), which represents the additive amounts that should be added

| Stage | Process or material       | Time (minutes) |
|-------|---------------------------|----------------|
| 1.    | Mastication of TSR 20     | 5              |
| 2.    | ZnO                       | 1              |
| 3.    | Stearic acid              | 1              |
| 4.    | MBTS                      | 1              |
| 5.    | Sulfur                    | 1              |
| 6.    | Mixing for homogenization | 2              |

#### Table 2. NR compounding procedures

## Table 3. Total crosslink density and distribution of crosslink density of gum NR vulcanizates atdifferent ratios of sulfur to MBTS accelerator

|                       | Total Crosslink                     | Disulfide Cı                        | osslink            | Polysulfide (                       | Crosslink          |  |
|-----------------------|-------------------------------------|-------------------------------------|--------------------|-------------------------------------|--------------------|--|
| Sample Code           | Density                             | Densit                              | t <mark>y</mark>   | Density                             |                    |  |
|                       | <mark>(mol/g)</mark>                | <mark>(mol/g)</mark>                | <mark>(%)</mark>   | <mark>(mol/g)</mark>                | <mark>(%)</mark>   |  |
| A1(0.14)              | <mark>9.78 x 10<sup>-6</sup></mark> | <mark>3.62 x 10<sup>-6</sup></mark> | <mark>37.07</mark> | <mark>6.16 x 10<sup>-6</sup></mark> | <mark>62.93</mark> |  |
| <mark>A2(0.22)</mark> | <mark>1.75 x 10<sup>-5</sup></mark> | <mark>6.88 x 10<sup>-6</sup></mark> | <mark>39.36</mark> | <mark>1.06 x 10<sup>-5</sup></mark> | <mark>60.64</mark> |  |
| <mark>A3(1.11)</mark> | <mark>5.28 x 10⁻⁵</mark>            | <mark>2.00 x 10<sup>-5</sup></mark> | <mark>37.87</mark> | <mark>3.28 x 10⁻⁵</mark>            | <mark>62.13</mark> |  |
| A4(2.15)              | <mark>7.03 x 10<sup>-5</sup></mark> | <mark>1.94 x 10<sup>-5</sup></mark> | <mark>27.63</mark> | <mark>5.09 x 10⁻⁵</mark>            | <mark>72.37</mark> |  |

| Sample Code | $T_{\text{onset}}$ (°C) | $T_{\rm end}$ (°C) | Residu at 500°C (%) |
|-------------|-------------------------|--------------------|---------------------|
| A1(0.14)    | 350.5                   | 404.1              | 5.9                 |
| A2(0.22)    | 351.6                   | 402.4              | 5.9                 |
| A3(1.11)    | 348.4                   | 401.7              | 6.1                 |
| A4(2.15)    | 353.0                   | 409.3              | 8.4                 |

 Table 4 Thermal degradation temperature of gum NR vulcanizates at different ratios of sulfur to MBTS accelerator