

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

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Abstract

It is well-recognized that the sulfur to accelerator (S/A) ratio greatly influences the nature of rubber vulcanizates. Viscoelasticity, vibration damping, and thermal stability are important properties of rubber vulcanizates used in vibration isolators. This study aimed to assess the effects of sulfur to 2-2'-dithiobenzothiazole (MBTS) accelerator ratio on viscoelastic, vibration damping, and thermal stability of gum natural rubber (NR) vulcanizates. The viscoelastic and vibration damping properties were determined by using a rubber process analyzer (RPA), while the thermal stability was investigated by thermogravimetric analysis (TGA). The results showed that the gum NR vulcanizates prepared with a sulphur to MBTS accelerator ratio at 1.11 had the best viscoelastic and vibration damping properties for use as a rubber isolator. However, regarding thermal stability, the gum NR vulcanizates prepared with sulfur to MBTS accelerator ratio at 2.15 were superior to the others.

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

1. Introduction

Natural rubber (NR) is prominent plantation crop in Indonesia, but is not locally particularly popular material, and is not a high value product; it is a commodity. Therefore, there should be further development with diversification of NR products to increase their value and ramp up the domestic consumption rate. Rubber products have many potential uses, including use as vibration isolator or damper for seismic protection of buildings and flyover structures, in machinery, automobiles, and on shipboards (Polukoshko, Martinovs, & Zaicevs, 2018).

Vibration isolators or dampers are found in automotive applications. The rubber product demands align with developments in the automotive market. The products are developed based on material engineering to obtain optimum viscoelasticity, vibration damping, and thermal stability properties matching the material requirements. Good materials for vibration isolators are indicated by high damping factor, viscous modulus, thermal stability, and low elastic shear modulus (Pochivalov *et al.*, 2020; Zhou, Yu, Shao, Zhang, & Wang, 2016). NR has poorer vibration damping properties than synthetic rubber, with the smaller tangent delta or loss factor (Halladay & Jaglowski, 2017). Good damping materials for outdoors and machinery applications should exhibit a high loss factor or tangent delta ($\tan \delta \geq 0.3$) over a wide temperature range (Xiaozhen He, Ming Qu, & Xinyan Shi, 2016). The poor vibration damping is caused by the

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viscoelasticity having more of elastic component than of the viscous one, in the intrinsic molecular chain structure. Therefore, it's necessary to study ways to improve the vibration damping ability of NR.

The viscoelastic properties of rubber can be determined using dynamic property tests, such as in dynamic mechanical analysis (DMA) or in the rubber process analyzer (RPA). The results depend on both frequency and amplitude of strain, and also on temperature (Hentschke, 2017). The most important property that determines the vibration damping is hysteresis. The hysteresis is indicated by the tangent delta measurement. The types of raw rubber and compounding chemicals (Halladay & Jaglowski, 2017) are determinants of the rubber vulcanizate's hysteresis, and the most influential are the type and amount of filler materials (Halladay & Jaglowski, 2017), along with vulcanizing materials (Le Cam, 2017; Shi *et al.*, 2019), softeners or plasticizers (Halladay & Jaglowski, 2017) and resinous materials (Su, Zhao, Xu, & Zhang, 2015).

Polymer viscoelasticity is generally influenced by its molecular chain structure (Karl, Kirsch, Faderl, Perko, & Fras, 2020; Vašina, Pöschl, & Zádrapa, 2018) and main composition (Karl, Kirsch, Faderl, Perko, & Fras, 2020; Tolpekina, Pyckhout-Hintzen, & Persson, 2019; Vašina, Pöschl, & Zádrapa, 2018). The rubber molecules can be modified to change their vibration damping and viscoelastic properties (Halladay & Jaglowski, 2017; Lei, Zhang, Kuang, & Yang, 2019; Vašina, Pöschl, & Zádrapa, 2018). Engineering the molecular structure involves certain treatments that can change the number and type of sulfidic crosslinks formed between the rubber polymer molecules. The numbers and types of crosslinks between sulfides in the rubber vulcanizate are strongly affected by the ratio of sulfur to its accelerators (Larpkasemsuk, Raksaksri, Chuayjuljit, Chaiwutthinan, & Boonmahitthisud, 2019), while the density of sulfide crosslinks greatly affects properties of the rubber vulcanizate (Alshabat & Abouel-Kasem, 2021; Han *et al.*, 2020; Kim, Park, Lee, & Seo, 2020; Shi *et al.*, 2019). Some studies have reported on the vibration damping properties of NR. The studies employed some treatments that change the viscoelastic properties, such as manipulating the type and amount of filler, the softening agents, the sulfur vulcanization system, the rubber blend, or the addition of resin (Halladay & Jaglowski, 2017; Koupai, Bakhshi, & Tabrizi, 2017; Lei, Zhang, 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 molecular structure of NR was changed by the number and type of sulfide crosslinks, affecting its viscoelastic (and especially vibration damping) properties.

Table 1. Gum NR compounding formulations

Sample code	Material component					
	TSR 20	ZnO (phr)	Stearic Acid (phr)	Sulfur (phr)	MBTS (phr)	Ratio (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 abbreviation means parts per hundred rubber (phr), used to represent the additive amounts

This study assessed the characteristics of viscoelastic properties, vibration damping, and thermal stability for gum (i.e., not filled) NR vulcanizates. The influence of the ratio of sulfur to MBT accelerator on viscoelastic, damping, and thermal stability properties of gum NR vulcanizates is explored in detail, to identify a natural rubber compound design that fits the requirements of vibration isolators or dampers in automotive applications (requiring resistance to thermal degradation).

2. Materials and Methods

2.1 Materials

The rubber compound was made by mixing NR subtype SIR 20 (TSR 20) as a raw elastomer with rubber compounding chemicals. These chemicals were as follows: 1) Zinc oxide (ZnO) UN 3077 from Lanxess, Germany (activating agent), 2) Aflux®52 from Lanxess Germany (stearic acid), 3) 2-2'-dithiobenzothiazole (MBTS) from Kemai, China (accelerator), and 4) Midas SP 325 sulphur from Miwon Co., Japan (vulcanizing agent). The entire chemicals for rubber compounding were tested and passed the technical quality check. The rubber compound formulations tested different sulfur doses, based on the MBTS accelerator that is related to the sulfur, and the formulations are displayed in Table 1.

Tetrahydrofuran (THF) and *n*-hexane were used for sample purification, then toluene was used for swelling samples. These solvents were obtained from Sigma-Aldrich. For determination of the crosslink density and distribution, 2-propanethiol ($\geq 98\%$), hexanethiol ($\geq 95\%$), and hexylamine ($\geq 98\%$) were provided by Sigma-Aldrich.

2.2 The production of rubber compound

The rubber compound was produced by mixing rubber with chemicals in a laboratory-scale open roll mill. It has a 1000 gram/batch capacity and is made by Berstorff, Germany. The ASTM 3182 standard is the basis of rubber mixing, with the procedure summarized in Table 2. In mastication, the natural rubber had its viscosity reduced to make it easier to mix in the chemicals. The already-masticated rubber will be smoother, known by the level of plasticity. Then, the chemicals are mixed in with the rubber. The first chemical is ZnO (zinc oxide), followed by stearic acid, the accelerator, and finally, the vulcanizing sulfur. The next step after the addition of chemicals is milling the natural rubber.

Table 2. NR compounding schedule

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

A sulfur to accelerator ratio below 0.3 is used in an efficient type sulfur vulcanization system. Next, rubber vulcanization of the semi-efficient type has a ratio between 0.4 and 2. Meanwhile, a conventional sulfur vulcanization system has a larger ratio than 2 (Bellander, 1998). Based on the criteria for the type of sulfur vulcanization system, the NR vulcanizations with a sulfur to MBTS accelerator ratio of 0.14 and 0.22 are efficient type, and the ratios of 1.11 and 2.0 are respectively of semi-efficient and conventional types.

2.3 Determining the curing characteristics

The ASTM D5289-12 standard was followed at 150°C with an Alpha Moving Die Rheometer (MDR) 2000 (Alfa Technologies, Akron, USA) for characterizing the rubber compounds' cure responses. Eventually, the characterizations determined to describe the rubber compound's curing were the maximum and minimum torque, the delta torque, the optimum curing time (t_{90}), and the scorch time (t_{s2}). Next, the so determined optimum cure time is used in molding the rubber compounds, which provides the test sample vulcanizates. The molding was done with a Japan-made hydraulic press (KMC).

2.4 Determination of the crosslink density and distribution

In this study, the crosslink density was determined by swelling measurement. Before determining the crosslink density of a rubber vulcanizate, organic additives and impurities were first removed by THF and *n*-hexane. The rubber vulcanizates (10 mm x 10 mm x 1 mm size) were immersed in *n*-hexane for 3 days and then in 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 measured. The proportions of each crosslink type were determined by using thiol-amine reactions through the selective cleavage of a certain sulfidic bond. Polysulfide cleavage was done by reacting the swollen vulcanizates with a solution composed of 2-propanethiol (0,4 M) and hexylamine (0,4 M) in toluene for 6 h at room temperature under N₂ atmosphere. Cleavage of disulfide and polysulfide bonds was achieved by reacting the swollen vulcanizates with a solution composed of hexanethiol (2.0 M) and hexylamine (4.0 M) in toluene for 12 h at room temperature under N₂ atmosphere (Choi & Kim, 2015). After the thiol-amine reactions were completed, the vulcanizate was immersed in toluene for 24 h. Afterward, it was moved to fresh toluene and again immersed for 24 h. After the final immersion in toluene, determination of the crosslink density was performed on the swollen vulcanizates. The weights of

the swollen vulcanizates were measured and the crosslink densities (V) were calculated using the Flory-Rehner equation (1).

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

where V_r is the volume fraction of the crosslinked polymer, χ is the interaction parameter between the polymer and solvent, and V_1 is the molar volume of the swelling solvent (106.27 cm³/mol for toluene). The V_r is determined by equation (2).

$$V_r = \frac{\frac{(W_0 - W_f)}{\rho_r}}{\frac{(W_0 - W_f)}{\rho_r} - \frac{(W_0 - W_a)}{\rho_s}} \quad (2)$$

where W_0 (g) is the weight of the rubber sample before swelling, W_f (g) is the weight of the filler, W_a (g) is the weight of the rubber sample after swelling, ρ_r (g/cm³) is the density of rubber, and ρ_s (g/cm³) is the density of solvent.

2.5 Testing the dynamic and vibration damping properties

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

2.6 Thermal property testing

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

3. Results and Discussion

3.1 Curing characteristics of rubber compound

The maximum torque (M_H) and minimum torque (M_L), as well as the difference between M_H and M_L (or the delta torque), the optimum curing time (t_{90}), and scorch time (t_{s2}), are the key curing characteristics of a rubber mix. They were determined by a rheometer and used to obtain data for processing to finished rubber products. 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

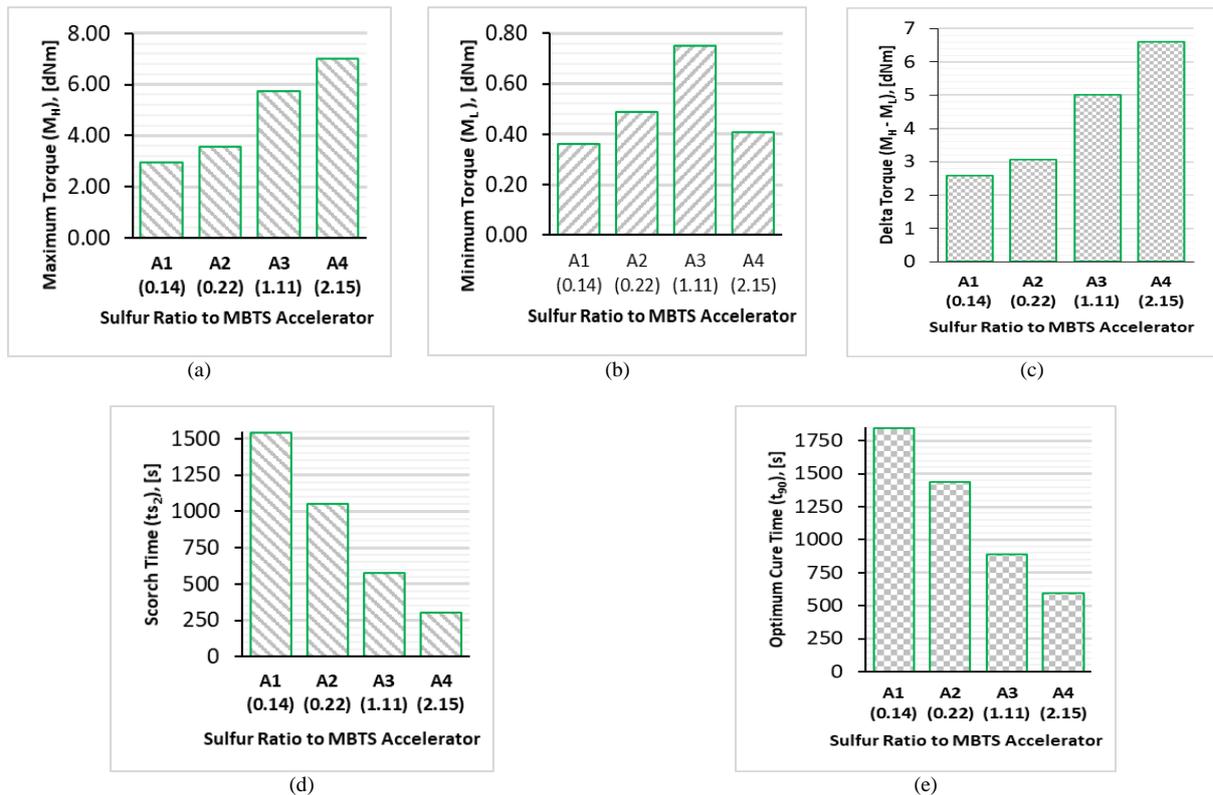


Figure 1 Curing characteristics of gum NR compounds prepared at different ratios of sulfur to accelerator, (a) maximum torque, (b) minimum torque, (c) delta torque, (d) scorch time, and (e) optimum cure time.

scorch time) were greatly affected by the ratio of sulfur to the MBTS accelerator. This ratio is connected to the type of bonds formed in the rubber vulcanizates. The gum NR compounds with sample codes A1(0.14), and A2(0.22) had efficient sulfur vulcanization. Meanwhile, the samples A3(1.11) and A4(2.15) had semi-efficient and conventional sulfur vulcanization. Increasing the ratio of sulfur to MBTS accelerator will increase the maximum torque (M_H) and the delta torque ($M_H - M_L$). It can also affect optimum cure (t_{90}) and scorch (t_{s2}) times. The maximum torque (M_H) of a rubber compound indicates the maximum crosslinking that can form during vulcanization (Shi *et al.*, 2019), while the minimum torque (M_L) is the mixture's viscosity indicator and provides information related to the rubber compound's processability (Hiranobe *et al.*, 2021). Figure 1(a) shows that the maximum torque increased with the ratio of sulfur to MBTS accelerator. The minimum torque in all cases of gum NR compounds (Figure 1(b)) was reasonably unchanged (0.3 to 0.8 dNm). Figure 1(a) also illustrates that the maximum number of crosslinks increased with the sulfur to accelerator ratio. It is correlated with an increased maximum torque.

Another curing characteristic of rubber compounds is the 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 for the polymer chains. A larger 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 increased with the ratio of sulfur to accelerator. The gum NR compound's delta torque, after use of a conventional sulfur vulcanization system, tended

to have higher values than the ones from semi-efficient or efficient sulfur vulcanization.

Figures 1(d) and 1(e) indicate that increasing the ratio of sulfur to MBTS accelerator can maximize the optimum cure time (t_{90}) and push the scorch time (t_{s2}) at a specified vulcanization temperature. Increasing the amount of sulfur in the rubber compound can speed up and reduce the reaction time for crosslink formation.

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 densities were greatly affected by the ratio of sulfur to MBTS accelerator. From these results, it can be seen that no monosulfide cross-links were observed. It is concluded that the NR vulcanization system with sulfur and MBTS did not form monosulfide cross-links. For the MBTS accelerator cure system, after immersion in the chemical probe solution for polysulfide and disulfide cleavage, the NR vulcanizate was dissolved.

Increasing the ratio of sulfur to MBTS accelerator will increase the total crosslink density and polysulfide crosslink density. The disulfide crosslink density increased up to a sulfur to MBTS accelerator ratio of 1.11, and after that, the density decreased. The sulfur in rubber vulcanization acts as a crosslinking agent, and a larger amount of sulfur added to the natural rubber compound will also increase the total crosslink density, but the increase is not proportional to the total crosslink density and the distribution of crosslink

Table 3. Total crosslink density and its distribution by crosslink type, in gum NR vulcanizates prepared at different ratios of sulfur to MBTS accelerator.

Sample code	Total crosslink density	Disulfide crosslink density		Polysulfide crosslink density	
	(mol/g)	(mol/g)	(%)	(mol/g)	(%)
A1(0.14)	9.78×10^{-6}	3.62×10^{-6}	37.07	6.16×10^{-6}	62.93
A2(0.22)	1.75×10^{-5}	6.88×10^{-6}	39.36	1.06×10^{-5}	60.64
A3(1.11)	5.28×10^{-5}	2.00×10^{-5}	37.87	3.28×10^{-5}	62.13
A4(2.15)	7.03×10^{-5}	1.94×10^{-5}	27.63	5.09×10^{-5}	72.37

density. Boonkerd *et al.* (2016) stated that the percentage of polysulfide crosslinks was not proportional to the sulfur to accelerator ratio.

3.3 Characteristics of viscoelastic and vibration damping properties

We consider natural rubber a viscoelastic material: having a combination of viscous and elastic properties. The rubber's viscoelastic behavior can be assessed through testing the properties, and it depends on both frequency and amplitude of the strain and also on the temperature (Hentschke, 2017). The viscoelasticity gives hysteresis loops in the dynamic property measurements (Halladay & Jaglowski, 2017; Koupai, Bakhshi, & Tabrizi, 2017). Hysteresis is quantified by the amount of energy spent during rubber deformation, which we determine per cycle. Later, the hysteresis determines the dissipating ability (conversion of mechanical energy to heat) during vibrations of the rubber material (Halladay & Jaglowski, 2017). Tangent delta or loss factor measures the hysteresis phenomenon to show the energy dissipation capacity of a viscoelastic material subjected to deformation cycles. This energy dissipation affects the mechanical vibration damping capacity. A larger tangent delta means better vibration damping capacity. The tangent delta can be defined by the ratio of viscous to elastic shear modulus.

The Rubber Process Analyzer (RPA) is a testing tool that functions like a strain-controlled rotational shear rheometer. The dynamic properties of gum NR compounds were examined with different ratios of sulfur to MBTS accelerator. The properties were determined using the RPA. The dynamic properties can be extracted from the response profile showing the relationships among elastic shear modulus, viscous modulus, and complex shear modulus, by frequency. The vibration damping properties of gum NR compounds were assessed from the tangent delta versus frequency. Based on the dynamic property test, using RPA at a temperature of 90°C (as shown in Figure 2), the gum NR compounds with different ratios of sulfur to MBTS accelerator had similar profiles of the dynamic properties versus frequency (elastic shear modulus, viscous modulus, and complex shear modulus). The gum NR compound with a sulfur vulcanization system that is semi-efficient (code A3(1.11)) shows a drastic change in the elastic absolute value (Figure 2(a)) and in complex shear modulus (Figure 2(c)) towards lower values starting at a frequency of 3.3 Hz. There is also a shift in the viscous modulus (Figure 2(b)) towards higher values starting at a frequency of 25 Hz. The gum NR

compounds with the efficient (A1(0.14) and A2(0.22)) and conventional (A4(2.15)) type sulfur vulcanization systems had relatively small shifts in the dynamic properties.

Figure 2(d) shows the vibration damping properties of the gum NR compounds prepared with different ratios of sulfur to MBTS accelerator, represented by tangent delta versus frequency relationships. The gum NR compound using a semi-efficient sulfur vulcanization system (code A3(1.11)) has a significant shift in the tangent delta towards higher values starting at a frequency of 4.6 Hz. The gum NR compounds with efficient (A1(0.14)) and A2(0.22)) and conventional (A4(2.15)) sulfur vulcanization have relatively small shifts in tangent delta. The response of tangent delta to frequency from RPA testing indicates that the gum NR compound prepared with semi-efficient sulfur vulcanization has better vibration damping properties than those with efficient or conventional vulcanization. This means that the gum NR compound using semi-efficient sulfur vulcanization had more viscous properties than elastic properties in its response to deformation. According to the results in Table 3 and Figure 2(d), there is a correlation between the distribution of crosslinks and the vibration-damping properties of rubber 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 polysulfide crosslinks contribute to the flexibility of rubber vulcanizates. The gum NR compound using a semi-efficient sulfur vulcanization system (code A3(1.11)) had higher disulfide crosslink density (Table 3) and the tangent delta (Figure 2(d)) than with efficient or conventional vulcanization. The disulfide crosslinks are predicted to contribute more to the viscous properties than to the elastic properties of the rubber. In contrast, the polysulfide crosslinks are predicted contribute more to the elastic properties.

If carbon black is loaded to fill the NR compound, the viscoelastic properties will be affected. According to Pöschl *et al.* (2020), the damping of mechanical vibrations is influenced by the carbon black type and amount. The stiffness and hardness of rubber vulcanizates generally increases with the loading level of carbon black filler. This increases elasticity and reduces the damping characteristics.

3.4 Thermal stability properties

In this study, thermogravimetric analysis (TGA) was applied to assess the thermal stability or thermal degradation behavior of gum NR vulcanizates prepared with different ratios of sulfur to MBTS accelerator. The thermal stability of the material is observed at various ratios of sulfur

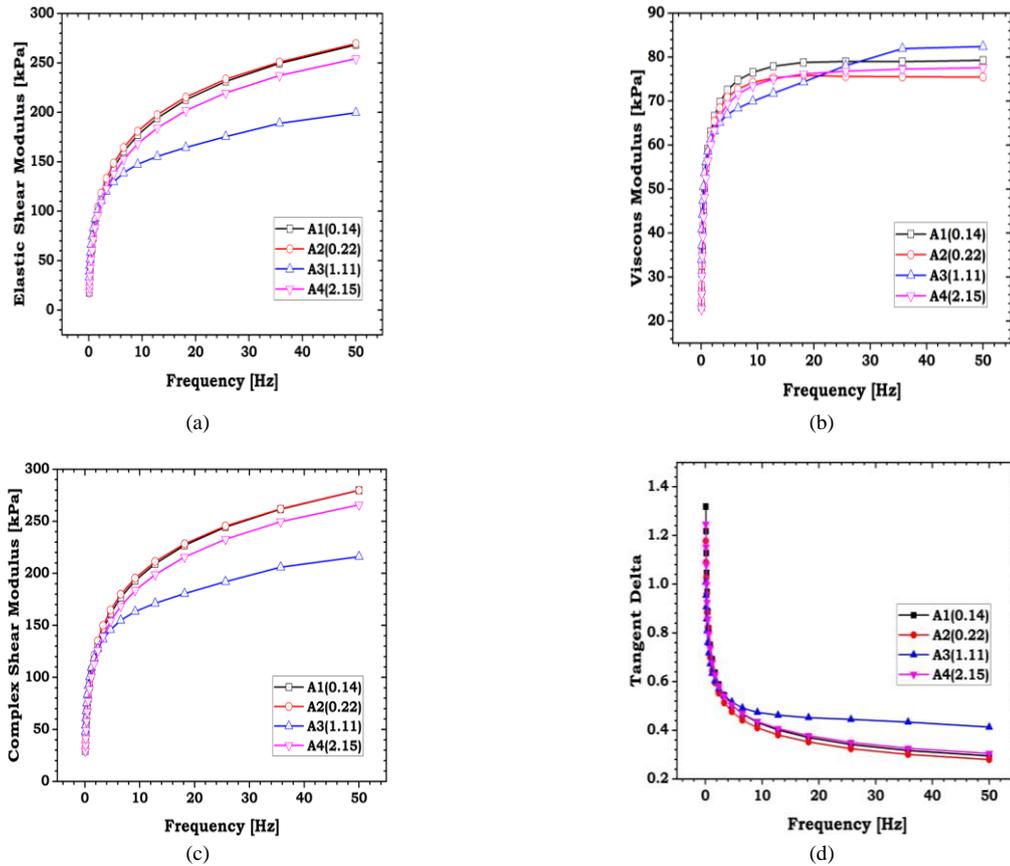


Figure 2. Dynamic mechanical responses to frequency of the gum NR compounds prepared at different ratios of sulfur to the accelerator: (a) elastic shear modulus, (b) viscous modulus, (c) complex shear modulus, and (d) tangent delta.

to MBTS accelerator (0.14; 0.22; 1.11; and 2.15). The sulfur to accelerator ratio determines the type of sulfur vulcanization system.

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 balance in the gum NR vulcanizates. Then, the experimental runs also reveal the start and end of the decomposition processes. For the four samples, T_{onset} and T_{end} are summarized in Table 4. The gum NR vulcanizate with 2.15 ratio of sulfur to MBTS (conventional system) had a higher degradation temperature than the other NR vulcanizates tested in this study: it had better thermal stability than NR vulcanizates with an efficient system (ratio of 0.14 or 0.22). This finding is different from prior studies, in that natural rubber vulcanizates prepared with efficient sulfur vulcanization have had better thermal stability than those with conventional or semi-efficient sulfur vulcanization systems (Hayeemasae & Masa, 2020; Larpkasemsuk, Raksakri, Chuayjuljit, Chaiwutthinan, & Boonmahitthisud, 2019). The difference may be due to the choice of accelerator. Each accelerator can produce a different distribution of crosslink types (monosulfidic, disulfidic, or polysulfidic crosslinks), even with fixed amounts of sulfur and of accelerator (Boonkerd, Deeprasertkul, & Boonsomwong, 2016).

The thermal degradation of natural rubber vulcanizates involves scission of those bonds. The

polysulfidic bond has a strength of less than 262 kJ/mol, while the monosulfidic bond has 280 kJ/mol (Hayeemasae & Masa, 2020). The sulfur to accelerator (S/A) ratio can influence the numbers by type of crosslinks formed. More monosulfidic bonds would be expected to give a better thermal stability. The monosulfidic, disulfidic, and polysulfidic crosslinks affect the thermal stability. The thermogram curve presented in Figure 3(b) show gum NR vulcanizates' temperatures with conventional (regular) system of sulfur vulcanization tending to be more heat stable than the others in this experiment. The initial degradation occurs at 353°C, and the final degradation is at 409.3°C.

4. Conclusions

Based on the findings we conclude that:

The maximum torque (M_H), the difference between maximum and minimum torques ($M_H - M_L$), and the optimum curing time (t_{90}), as well as the scorch time (t_{s2}), tended to increase with the ratio of sulfur to MBTS accelerator, in compounding formulation for unfilled gum NR compounds.

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

The gum NR vulcanizates having a sulfur to MBTS accelerator ratio of 1.11 had better viscoelastic and vibration

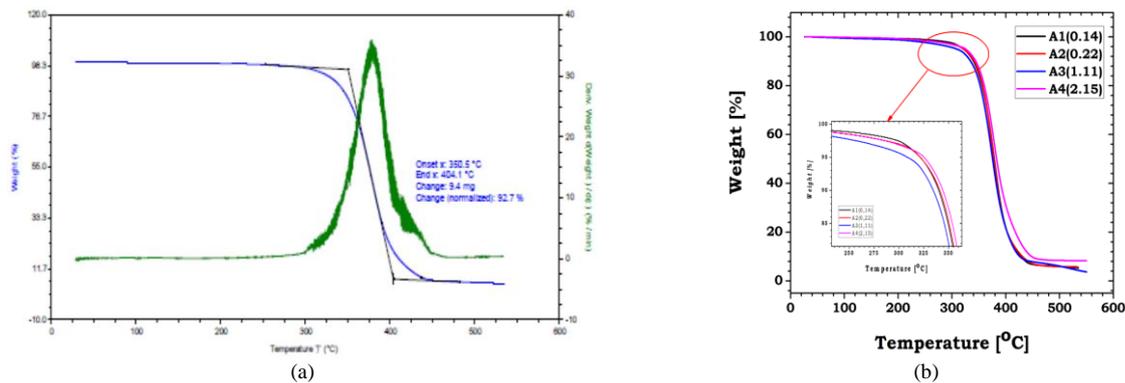


Figure 3. TGA curves for the gum NR vulcanizates (a) in one case, (b) for all four samples prepared with various ratios of sulfur to the accelerator.

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

Sample Code	T_{onset} (°C)	T_{end} (°C)	Residue 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

damping properties than the others tested, for use as vibration damping material in automotive applications.

The gum NR vulcanizates prepared with a sulfur ratio to MBTS accelerator ratio of 2.15 had the best thermal stability among the cases tested.

Using semi-efficient sulfur vulcanization in gum rubber vulcanizates with an S/A ratio of 1.11 was preferable for vibration isolators in automotive applications, but the thermal stability needs to be improved.

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