The rheological and mechanical properties of natural rubber/graphene composites

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Abstract. This research focuses on the use of graphene as a filler for natural rubber (NR). The purpose of using graphene is to improve the mechanical properties of rubber compounds and their processing characteristics. Graphene (G) consists of carbon atoms and is an essential filler for polymers to enhance electrical and mechanical properties. The addition of graphene to rubber can improve the wear resistance and mechanical strength of rubber products. Thus, the effect of the graphene filler composition is interesting to study. Variety of graphene loads (10, 20, and 30 part hundred rubber (phr)) were combined with a variety of sulfur fillers (S) (10 and 20 phr) and then composited with natural rubber. The effect of variations in a load of graphene and sulfur fillers on the rheological properties, abrasion resistance, and compression set were studied. The results showed that the optimal combination of the G/S load variation was 20/10 phr. It leads to a more extraordinary strengthening ability that is binding rubber molecules so that the interactions occurred, both physical and chemical, could be formed better with the NR molecular chain. This resulted in distinct rheological properties enhancement such as torque modulus and curing time. In contrast, the mechanical properties like abrasion resistance and compression set were still good. The FTIR Spectra of natural rubber-graphene composites confirmed that good filler disperses were obtained due to several intramolecular interactions of carbon graphene with NR molecules. Graphene can be used as a filler for rubber products, mainly rubber, abrasion, and compression resistant, and an alternative for commercial fillers.

1. Introduction
One of the essential materials used widely in the rubber finished goods industry is natural rubber. Its main advantages are elasticity and ease of processing. In addition, natural rubbers' characteristics are reusable, environmentally friendly, and biodegradable, making their demand high worldwide [1]. However, raw rubbers are rarely used in their original forms for all types of applications. In the making process, rubbers include the addition of many supporting substances known as additives. The addition of additives ensures the rubber compound can be processed optimally and, when vulcanized, will improve rubber product application properties.

The most used content of additive in rubber industries is carbon black. However, carbon black application has a drawback, the adhesive of the compound decreases. Although carbon black didn't match the other substances when mixing, a few types of research showed a small amount of particulate, such as carbon black, which could change rubber's mechanical and physical properties [2].

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Another alternative material for carbon black in the making of rubber products is graphene. Graphene is essential for polymers for increasing electrical, mechanical, or barrier properties due to the good mechanical, low density, high thermal conductivity, and electrical mobility [3-4]. In addition, graphene could spread evenly in rubber poles because it contains oxygen, so the interaction between rubber molecules becomes stronger.

Research about graphene has been carried out. One of them studied graphene or graphene oxide as a nanofiller for vulcanization of nano rubber composite, resulting in significantly improved mechanical properties and gas-barrier performance, thermal stability, electric conductivity, anti-oxidation ability as well as some functionalities [5]. The research about natural rubber-graphene-silica composites showed favorable mechanical properties and low air vapor permeability, sound gas barrier, excellent wear resistance, and low rolling resistance, making graphene oxide-silica-Styrene Butadiene Rubber very competitive for environmental friendly tires [6,7]. Research [8], graphene substitute for carbon black on rubber products, offered higher hardness, modulus, and wear resistance than carbon black filler. Research of rubber silicon-graphene composite used as strain sensor has been done to detect seal rubber's operational condition [9]. Graphene-based filler addition into several rubber matrices could significantly increase the rubber nanocomposites' mechanical, electrical, dynamic-mechanical, thermal, and barrier properties [10].

To the author's knowledge, there has been no research on graphene-NR composites that have investigated the mechanical properties, especially the compression set and abrasion resistance of the composites. So, by knowing these properties, rubber products can be made that are resistant to friction and compression. In this research, graphene-NR composite's rheological and mechanical properties were studied, using different variations of graphene and sulfur. First, the graphene-NR composite properties were analyzed and compared with carbon black-NR composite as a current commercial rubber compound. Then filler dispersion on rubber matrix was characterized by using Fourier Transform Infrared (FTIR).

2. Materials and methods

2.1. Materials

Materials used in this research are natural rubbers type Standard Indonesian Rubber-20 (SIR) obtained from PT. Prasidha Aneka Niaga, Tbk. Meanwhile, the technical quality rubber chemicals which were used on the rubber compound formula were described as follows. Graphene was bought from the supplier of PT. Multi Citra Chemindo Nusa, Indonesia. Zinc oxide (ZnO), stearic acid, minarex oil, tetramethylthiuram disulfide (MBTS), tetramethyl thiuram disulfide (TMTD), N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), trimethyl quinon (TMQ), sulfur, kaolin and pre vulcanization inhibitor (PVI) were obtained from the supplier of PT. Brataco Chemical, Indonesia.

2.2. Mixing and Rubber Compounding

The first step was weight measurement of all required materials following the formulations in Table 1. Meanwhile, experimental treatment by varying graphene (G) filler and Sulfur (S) vulcanisator (G/S), 10/5; 20/5; 30/5; 10/10; 20/10; 30/10 phr, and as a reference, a commercial rubber compound with carbon black (CB) filler was used.

They mixed on open two roll mill XK-160 type (Shanghai Rubber, China), using the following steps: mastication SIR 20 (NR) until the texture was plastic. Then, mixing graphene filler, antioxidant IPPD and TMQ, activator ZnO and stearic acid, accelerator TMTD and MBTS and Sulfur as vulcanisator, each ground until homogenized mixing from 2 to 3 minutes long. Subsequently defined compound sheet thickness for 2 mm, later put it on transparent plastic. Finally, the compound became vulcanized, inserted into molding using a hydraulic heating press (YG-220, Shanghai Rubber Machine Worker, China) at a temperature of 145°C for 5 minutes.
Table 1. Rubber compound formulations.

| Material        | Composition (per hundred rubber, phr) | G/S   | CB |
|-----------------|---------------------------------------|-------|----|
|                 |                                       | 10/5  | 20/5 | 30/5 | 10/10 | 20/10 | 30/10 |
| SIR 20 (NR)     |                                       | 100   | 100  | 100  | 100   | 100   | 100   |
| Graphene        |                                       | 10    | 20   | 30   | 10    | 20    | 30    |
| Kaolin          |                                       | 20    | 20   | 20   | 20    | 20    | 20    |
| ZnO             |                                       | 5     | 5    | 5    | 5     | 5     | 5     |
| Stearic acid    |                                       | 2     | 2    | 2    | 2     | 2     | 2     |
| Carbon black    |                                       | -     | -    | -    | -     | -     | -     |
| IPPD            |                                       | 2     | 2    | 2    | 2     | 2     | 2     |
| TMQ             |                                       | 1     | 1    | 1    | 1     | 1     | 1     |
| MBTS            |                                       | 2     | 2    | 2    | 2     | 2     | 2     |
| TMTD            |                                       | 0.5   | 0.5  | 0.5  | 0.5   | 0.5   | 0.5   |
| Sulfur          |                                       | 5     | 5    | 5    | 10    | 10    | 10    |
| PVI             |                                       | 0.5   | 0.5  | 0.5  | 0.5   | 0.5   | 0.5   |

2.3. Testing and characterization

The vulcanization characteristics included Minimum Torque Modulus (MH), Maximum Torque Modulus (ML), optimum vulcanization time (t90), and scorch time (ts2), measured by using Moving Die Rheometer (MDR) at temperature 150°C according to ISO 3417. Testing for mechanical properties, including abrasion resistance and compression set parameters.

Abrasion resistance was tested according to ASTM D.241 and 241 the compression set was tested according to ASTM D 395-03. The rubber sample was pressed until its 25% initial thickness at 70°C and 100°C for up to 48 hours. Fourier Transform Infrared Spectroscopy (FTIR) was used for analyzing the phases that occurred in the process. FTIR from Tensor 27 was held on transmission mode at room temperature. Spectral gained at wavelength 3800-600 cm⁻¹. The evaluation of the spectrum followed to ASTM E1252-98 procedure.

3. Result and discussion

3.1. Rheological properties

Rheology of the Graphene/NR shown by using rheometer equipment. Test by rheometer represents curing characteristics data for each compound, including maximum (MH) and minimum torque (ML), torque delta (ΔM = MH - ML), scorch time (ts2), and optimum vulcanization time (t90). Curing characteristics of graphene/NR composite with a variation of G/S treatments obtained from the rheometer graph are represented in table 2.

Table 2. Curing characteristics of graphene/NR composite.

| Sample   | MH (kg-cm) | ML (kg-cm) | ΔM (kg-cm) | t90 (Min) | ts2 (Min) |
|----------|------------|------------|------------|-----------|-----------|
| G/S 10/5 | 0.38       | 11.57      | 11.95      | 5.63      | 3.58      |
| G/S 20/5 | 0.40       | 16.55      | 16.95      | 4.59      | 2.34      |
| G/S 30/5 | 1.08       | 17.99      | 19.07      | 4.44      | 2.05      |
| G/S 10/10| 1.11       | 27.57      | 28.68      | 3.60      | 1.67      |
| G/S 20/10| 1.67       | 30.18      | 31.85      | 3.48      | 1.15      |
| G/S 30/10| 1.54       | 29.02      | 30.56      | 3.71      | 1.29      |
| Carbon Black (CB) | 1.70 | 30.32 | 32.02 | 3.45 | 1.11 |

According to table 2, observation result from curing characteristics of graphene/NR shows that loading G/S variation increased maximum, minimum, and delta torque at each treatment. In general, the
rubber compound's torque modulus tended to rise until it reached a maximum value. It then dropped, which can be understood that the more the concentration of graphene, the more the minimum and maximum torque of the rubber compound. This result shows that additive substances mixing with the rubber matrix will generate a higher viscosity and modulus of the rubber composite. It appears that graphene had a more significant influence on the minimum torque (ML) and maximum torque (MH) enhancements. Graphene is an allotrope of carbon, has an excellent performance due to its unique structure, having a high surface area (2600 m²/g) [11,12]. The high additive surface area can absorb more rubber double bonds at the surface. Therefore, rubber bonds and become more extensive, so the maximum torque is high [13]. Other than that, the amount of sulfur ratio added can affect the forming of polysulfide cross-links (C-Sx-C) and disulfide (C-S-S-C) compared with monosulfide (C-S-C) [14] hence, makes the delta torque (ΔM) higher. This result shows that there were more cross-links formed. The value of torque modulus may indicate that many cross-links are included due to vulcanization [15, 16].

Table 2 shows that the more G/S loading, the lesser curing rate and reaches an optimum value at G/S 20/10 phr, with 3.48 minutes and scorch time 1.15 minutes. Table 2 shows that the more G/S loading, the lesser curing rate and reaches an optimum value at G/S 20/10 phr, with 3.48 minutes and scorch time 1.15 minutes. This result was influenced by the number of cross-links formed because the amount of sulfur used is a lot, so that the vulcanization time ran faster. In addition, as filler loading increased, mixing the filler into the rubber matrix also increased and consequently produced more heat due to additional friction. The scorch time indicates when the rubber compound can be processed at a specific temperature before the rubber compound's initial curing time to form cross-links[17]. The scorch time that is too long can increase the compound's viscosity, making it difficult for further processing. Therefore, the shorter the scorch time, the easier it would be for the rubber product processing [18].

At the G/S 20/10 composite load, both scorch time and the optimum curing time were shorter than the other G/S composites. Because of the high surface area, the viscosity was the highest and reached optimal for G/S 20/10 treatment. Moreover, giving the optimal shortest scorch and curing time [19]. At the low load, the probability of aggregate forming was smaller than the high additive load, and consequently, a good fill dispersion was achieved.

Based on the results, rheometric cure parameters showed G/S 20/10 phr composition has the best value, making it possible for the best interaction and distribution at G/S 20/10 phr treatment with NR matrix. Furthermore, rheological properties of G/S 20/10 phr had similarities with commercial compound carbon black/NR composite (table 2).

3.2. Mechanical properties

3.2.1. Compression set. Parameter compression set describes the ability of the Graphene/NR composite to return to its original size after getting pressure from a prolonged load at a specific temperature and time [20]. Low compression set values provide better deformation resistance of Graphene/NR composites as this is considered the highest elasticity level.

The compression set tended to rise with the increasing graphene load. This result might be because of the lousy interaction between rubber and additives on the matrix, and the cross-linking decreased. High additives loading also causes increasing in stiffness, increasing compression set [21]. The higher the G/S load, the compression set tended to decline. It indicated that Graphene/NR composite vulcanisates had good compression resistance due to the graphene's high surface area. Increased surface area increases the capacity to connect to elastic particles, although it has more interface cross-links so that vulcanisates do not deform easily [22]. On the other side, an increasing amount of sulfur increases compression that is defined as seen in figure 1. At Sulfur 5 phr loading, the total cross-link density formed from the vulcanization process is low. Therefore, the amount of cross-links resisting compressive force is far less than composites with high Sulfur loading.
In general, the compression set provides less value at 70°C than it did at higher temperatures (in this case, 100°C). It was primarily caused by chain-breaking at low temperatures, which resulted in physical damage, such as the inability to withstand compressive force. When thermal degradation was taken into account, the effect becomes worse at high temperatures. High-temperature degradation, particularly oxidative aging, will cause molecular rubber chains to break, cross-link, or modify the filler-rubber interface [23]. Chain cutting might take precedence, resulting in fewer cross-links. As a result, the number of broken cross-links equaled the amount of physical damage and thermal degradation. It caused compression to be set to a high value, resulting in a stiff graphene/NR composite. G/S 20/10 compression set to 70°C with the lowest value of 20.50 percent. This value was not significantly different from the commercial carbon black/NR composite compression set, which had a compression rate of 20.24 %.

3.2.2. Abrasion Resistance. Abrasion resistance is the strength of rubber to prevent friction in its use with other objects. The abrasion resistance value of graphene/NR composite is shown in figure 2.

The graph above (figure 2) shows that the abrasion resistance value is lower as the G/S loading increased and reached optimal G/S 20/10 treatment. It can be understood that graphene/NR composite rubber's ability to deal with mechanical behavior like rubbing, scraping, or erosive will increase. It was because, on that load, vulcanization had achieved a perfect vulcanization reaction. The sample bond structure became compact. It also became resistant to friction (abrasion) and interaction enhancement between additives and rubber molecules. Furthermore, graphene, which has a large surface area and small particle size, can play the role by connecting with NR macromolecular chain, having a reinforcement effect, spreading evenly in the matrix polymer, and forming a solid combination with
polymer chain [6, 24]. The higher the surface area, the smaller additive particles, showing more additive functional groups that bonded rubber molecules. The interaction between physical or chemical will be better [25], so the abrasion resistance will increase. The slightest abrasion resistance appeared in G/S 20/10 treatment with a value of 262.5 DIN mm$^3$, showing high resistance to friction or abrasion. The abrasion resistance value is not significantly different from the abrasion resistance value of commercial rubber compound with carbon black filler, which is 243 DIM mm$^3$. The smaller the abrasion resistance value of vulcanisate, the better the vulcanisate characteristic because of resistance from friction [26].

3.3. FTIR Analysis

FTIR Spectra of functional groups of graphene/NR composite (G/S 10/5 and G/S 20/10) and carbon black/NR composite is presented in figure 3.

![FTIR spectra](image)

Figure 3. FTIR spectra of graphene/NR composite (3a. G/S 10/5; 3b. G/S 20/10) and carbon black/NR composite (3c).

According to figure 3a and 3b, the spectrum of graphene/NR composite (G/S 10/5 and G/S 20/10), carbon framework can be noticed at regions of 2970-2850 cm$^{-1}$ wavenumber, which were absorption characteristics for alkane and alkyl groups and related to CH$_2$ and –CH$_3$ bonds. It founded clearly for cross-link of graphene/NR composite. It was estimated to be caused by the interaction between molecules when vulcanization. The most common appearance of C–H absorption was the presence of three strong bands under 3000 cm$^{-1}$. The spectrum with the most substantial absorption capability was at 2925 cm$^{-1}$ wavenumber due to absorption from the CH$_2$ group, from the type of CH$_2$ asymmetry stretching. A spectrum that appeared at range 2955 to 2957 cm$^{-1}$ wavenumber was possibly caused by the absorption of the asymmetric stretch of the methyl group (CH$_3$). The appearance could see the absorption caused by the presence of an alkyl group of a characteristic band that corresponds to C–H in the region of wave numbers 1400–1300 cm$^{-1}$. This spectrum showed absorption at 1452 cm$^{-1}$ wavenumber, showing a methyl group with asymmetric bending vibration of CH$_3$ divided into (CH$_3$)$_2$=C dan (CH$_3$)$_3$–C groups.

The presence of a methylene group as a support for absorption at 2925 cm$^{-1}$ wavenumber could be seen by the appearance of a very sharp band at 1452 cm$^{-1}$ wavenumber. The band appeared as a result of the absorption of the CH$_2$ group with the CH$_2$ symmetric bending vibration. In a spectrum of the range 700–995 cm$^{-1}$ there was solid alkenes C-H group absorption. Meanwhile, at 1643 cm$^{-1}$ spectrum
showed a typical peak for carbon double bond (C = C), a typical peak for carbon double bond found in cis-1,4 polyisoprene from natural rubber [27]. FTIR Spectra of Carbon Black/NR composite at figure 3c showed the relevance to Graphene/NR (G/S 20/10) composite spectra figure 3b.

4. Conclusion
Graphene can be used as a filler for black carbon substitution. Rheological measurements showed that the graphene/NR composite could increase the modulus of torque and accelerate the curing time and scorch time, which was achieved at 20/10 G/S treatment. Mechanical properties such as compression set and abrasion resistance showed a decreasing trend with increasing graphene loading. The FTIR spectra showed peaks at the range of 2970–2850 cm⁻¹ wavenumber related with –CH₂ and –CH₃ bonds, which were founded for cross-linking of graphene/NR composites. It was estimated to be caused by intermolecular interactions during vulcanization. The results showed that the graphene/NR composite with a filler load of 20/10 phr G/S generally showed better rheological and mechanical properties compared to other G/S filler loads in this study. It also indicates that graphene/NR composites were quite comparable to carbon black/NR composites.

5. References
[1] Lee KC, Yusoff NAM, Othman N and Mohamad Aini NA 2017 *IOP Conf. Ser. Mater. Sci. Eng.* **223** (1)
[2] Li X, Li Z, Xia Y and Xia Y 2012 *Comput. Mater. Sci.* **55** 157–165
[3] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ and Stach EA 2006 *Nature* **442**(7100) 282–286
[4] Novoselov KS, Fal’ko VI, Colombo L, Gellert PR, Schwab MG, Kim K 2012 *Nature* **490**(7419) 192–200
[5] H. Zhang, W. Xing, H. Li, Z. Xie, G. Huang and J. Wu 2019 *Adv. Ind. Eng. Polym. Res.* **2**(1) 32–41
[6] Wang J, Zhang K, Fei G, Salzano de Luna M, Lavorgna M and Xia H 2020 *Polymers* **12**(11) 2549
[7] Mao Y, Wen S, Chen Y, Zhang F, Panine P and Chan TW 2013 *Sci. Rep.* **3** 1–7
[8] Sayed F, Parmar M and Auti S 2019 *Lect. Notes. Mech. Eng.* **8**(09) 323–331
[9] Yang H, Yao XF, Zheng Z, Gong LH, Yuan L and Yuan YN 2018 *Compos. Sci. Technol.* **167** 371–378
[10] Malas A 2017 *Progress in Rubber Nanocomposites* (United Kingdom: Elsevier) 179–229
[11] Lee C, Wei X, Kysar JW and Hone J 2008 *Science* **321**(5887) 385–388
[12] Soldano C, Mahmood A and Dujardin E 2010 *Carbon N Y* **48**(8) 2127–2150
[13] Hasan A, ... H and Hongkokusumo S 2013 *J. Technol. Ser.* **16**(2) 109–115
[14] Fan RL, Zhang Y, Li F, Zhang YX, Sun K and Fan YZ 2001 *Polym. Test.* **20**(8) 925–936
[15] Ahmed K, Sirajuddin Nizami S, Zahid Raza N and Shirin K 2012 *Adv. Mater. Phys. Chem.* **02**(02) 90–97
[16] Manna, AK, De PP, ... Tripathy DK 1997 *Rubb. Chem. Technol.* **70**(4) 624–633
[17] Ngamsurat S, Boonkerd K, Leela-Adisorn U and Potiyaraj P 2011 *Energy Procedia* 452–458
[18] Handayani H 2014 *J. Penelit. Karer* **32**(1) 74
[19] Sareena C, Ramesan MT and Purushothaman E 2012 *J. Reinf. Plast. Compos.* **31**(8) 533–547
[20] Rajan R, Varghese S and George KE 2012 *Plast. Recycl. Technol.* **28**(4) 201–220
[21] Vishvanathperumal S and Gopalakannan S 2019 *Silicon* **11**(1) 117–135
[22] Maridass B and Gupta BR 2006 *J. Elastomers. Plast.* **38**(3) 211–229
[23] Maiti A, Gee RH, Weisgraber T, Chinn S, and Maxwell RS 2008 *Polym. Degrad. Stab.* **93**(12) 2226–2229
[24] Findik F, Yilmaz R and Köksal T 2004 *Mater. Des.* **25**(4) 269–276
[25] Prasetya HA, Marlina P and Widijajanti R 2020 *AIP Conf. Proc.* **2237** 020042
[26] Ulfah IM, Fidyaningsih R, Rahayu S, Fitriani DA, Saputra DA and Winarto DA 2015 *Procedia
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[27] Chalid M, Husnil YA, Puspitasari S and Cifriadi A 2020 Polymers (Basel) 12(12) 1–19