Dimethyl Ether (DME) and DME/LPG mixtures resistance characteristics of modified natural rubber compounds

H Handayani¹*, A Cifriadi¹, A Ramadhan¹, A F Falaah¹, N Hermawan² and E Yuliarita²

¹Research Center for Rubber Technology, Indonesian Rubber Research Institute, Bogor 16128, West Java, Indonesia
²Research and Development Centre for Oil and Gas Technology "LEMIGAS", South Jakarta 12230, Indonesia

* E-mail: hani.ppkbogor@gmail.com; emiy@lemigas.esdm.go.id

Abstract. The use of Liquified Petroleum Gas (LPG) in Indonesia is quite high, the volume reaches 6.7 million tons per year. Indonesia currently still imports 70% of its domestic consumption of LPG, or about IDR 40 trillion. Imports of Liquid Petroleum Gas (LPG) continues to increase every year. Dimethyl ether (DME) is one alternative to renewable fuels because its availability in the country is quite abundant. When DME applied as household fuels, some components such as metals and rubber should include resistance to DME, such as stoves, rubber hoses, rubber components in regulators and tube valves. Lemigas has succeeded in developing a DME resistant stove but still not found a rubber that is resistant to DME. This research aims to find a natural rubber formula that is resistant to DME and DME / LPG mixture. The study was conducted by varying the dose of sulphur (0.5, 1.5, and 3.5 phr) using 2 types of elastomer, Natural Rubber (NR) and Nitrile Butadiene Rubber (NBR). Immersion was carried out in DME and 3 variations of the DME/LPG mixture (10/90, 20/80, 30/70). The results showed that the compound formula using natural rubber with a sulphur dose of 1.5 phr has the best resistance to DME and DME/LPG mixtures.

1. Introduction
Imports of Liquified Petroleum Gas (LPG) continue to increase every year. Based on data of Pertamina, in 2016 Indonesia's LPG imports were around 66%, in 2017 it raised to 70% of the total LPG consumption of around 7.5 million metric tons (mt) per year. This increase was driven by an increase in public consumption, the conversion of kerosene to LPG in Eastern Indonesia, and the conversion of fuel to LPG for fishermen. On the other hand, domestic LPG production continues to decline due to declining production from domestic gas wells. Dimethyl ether (DME) is one of the materials that can be an alternative to new renewable fuels at this time because its availability in the country is quite abundant. DME is a type of renewable energy that could replace the use of fossil fuel in Indonesia [1]. As an alternative fuel, DME can be used to address energy security, energy conservation, and environmental concerns about the need for low carbon emissions [2, 3]. DME will be an important national energy security strategy due to the fact that Indonesia is rich in coal, natural gas, and biomass, which can be
used as raw materials to produce DME [4]. DME also has characters such as LPG that can be disbursed so that it is easy to distribute. DME can be used for blended mixed LPG with a variety of compositions and even replaces 100% LPG.

The use of DME in households is expected to reduce dependence on LPG to increase national energy security. From the results of a market trial conducted by Pertamina, DME when mixed with LPG at a composition of 50/50 produces a fire quality that is equivalent to LPG with better savings compared to LPG, therefore the opportunity to use DME as an alternative fuel substitute LPG is very large.

In line with this, it is necessary to produce supporting infrastructures such as tubes, regulators, hoses, and stoves that are resistant to DME or DME / LPG mixtures. Lembaga Minyak dan Gas (LEMIGAS) has obtained material that resistant to DME for tubes and regulators but has not yet found a formula for DME resistant rubber components. DME can cause degradation of rubber-based materials. The effect of the filler (carbon black) and plasticizer (minarex-B) components of vulcanized natural rubber has been examined [1]. Rubber components that are important and need to be renewed are the hose and rubber components contained in the regulator and tube valves (Figure 1). The rubber component contained in the tube valve consists of a rubber seal and rubber spindle. In the regulator, there are several rubber components, including rubber o-ring, valve bearings, and membrane (diaphragm) while the component that connects between the regulator and the stove is a rubber hose.

A study about the degradation of blending vulcanized natural rubber and nitrile butadiene rubber (NR/NBR) by dimethyl ether through variation of elastomer ratio using a blending of NR and NBR has been done by [5] and the study concluded that the increase of nitrile rubber (NBR) ratio of blending rubber vulcanized can reduce the tensile strength and elongation. In this experiment, we tried to use NR and NBR (in single-phase without blending each other) in variation of Vulcanization system to determine its resistance characteristic to DME and DME/LPG mixtures.

![Figure 1. Rubber component inside of regulator and tube valve of LPG.](image)

## 2. Materials and Methods

### 2.1. Materials

The materials used in this study include Natural rubber (NR), Standard Indonesia Rubber (SIR) 20 and Nitrile Butadiene Rubber (NBR) 3345 Krynac obtained from local suppliers, and also technical quality rubber compounding chemicals from local suppliers. The rubber compounding chemicals include sulphur Miwon SP-325 as vulcanization agent, stearic acid Aflux 52 and zinc oxide from Lanxess as activator, clay, and carbon black from Cabot as filler, CBS from Shandong and ZDBC from Willing as an accelerator, TMQ Vulkanox HS as an antioxidant, and antilux 654 as an antiozonant.

### 2.2. Compounding of Natural Rubber

Natural rubber and other ingredients were mixed in the two-roll open mill according to the compound formula in Table 1. The addition of chemicals uses a unit of phr (per hundred rubbers), this is used for
calculating formulas where other chemicals are calculated as parts per 100 weight of rubber. Compound formulated with variations in 2 types of elastomer and 3 doses of sulphur for 3 kinds of vulcanization system. The compounds were then cured in a press machine at 150 °C formed vulcanized rubber.

Table 1. The compound formula with varied kinds of elastomer and vulcanization system [6]

| Materials                                               | Dosage (per hundred rubber, phr) |
|---------------------------------------------------------|----------------------------------|
| NR (Natural Rubber)                                      | 100 100 100                      |
| NBR (Nitrile Butadiene Rubber) 3345                      | 100 100 100                      |
| Zinc oxide                                              | 5 5 5 5 5 5                      |
| Stearic acid                                            | 2 2 2 2 2 2                      |
| Clay                                                    | 100 100 100 80 80 80            |
| Carbon black N330                                       | 1 1 1 1 1 1                      |
| TMQ (2,2,4-Trimethyl-1,2-Dihydroquinoline)              | 2 2 2 2 2 2                      |
| Sulphur                                                 | 0.5 1.5 3.5 0.5 1.5 3.5          |
| CBS (N-Cyclohexyl-2-benzothiazole sulfenamide)          | 0.5 0.5 0.5 0.5 0.5 0.5          |
| ZDBC (Zinc dibutyl dithiocarbamate)                     | 1 1 1 1 1 1                      |

2.3. Curing Characteristic of Compound
Curing characteristic tested using Rheometer MDR 2000 according to ASTM D 2084-17 standard. Rheometer testing aims to determine the characteristics and time of vulcanization at a certain temperature of a rubber compound.

2.4. Mechanical and Physical Testing
Compression-molded sheets from the press molding were used to measure tensile strength, elongation at break, hardness, tear strength, and compression set. Each sample was cut into a dumbbell shape for the tensile test. The value of the tensile strength (MPa) and elongation at break (%) were measured using a LLOYD 2000R tensometer according to the ASTM D 412-16 standard. Hardness (Shore A) was measured using a Durometer, according to the ASTM D 2240-15 standard. Tear strength sample cut into angle shape and measured using a LLOYD 2000R tensometer according to the ASTM D 624-00(2012) standard. Compression set tested using compression set tester according to the ASTM D 395-16e1 standard. The properties such as hardness, tensile strength, and elongation at break were tested before and after ageing at 70 °C for 168h.

2.5. Immersion of rubber compound in DME and DME/LPG mixtures
The vulcanized rubber was immersed in DME and DME/LPG mixtures for 72 hours (3 days). The DME / LPG mixtures have been varied into 3 mixes, DME/LPG (10/90), DME/LPG (20/80), and DME/LPG (30/70). Each sample was cut into a dumbbell shape for tensile test. After immersion, each sample is calculated as a percent loss in weight and swelling volume. The data of swelling at those results is required as one of the standard physical testings of rubber products.

2.6. Loss in weight measurement
The vulcanized rubber samples were immersed in DME and DME/LPG mixture in a pressurized vessel (volume: 1.3 L). The mass change of these samples was investigated after the samples had been immersed in DME for 3 days and then exposed to room temperature for 24 hours [7]. The mass change is specified as a percentage (%), as shown in Equation 1 [8, 9, 10].
\[ \text{The mass change} \ (\%) = \frac{m_f - m_i}{m_i} \times 100\% \]  

(1)

where \( m_f \) (final mass) is the mass of the sample after it is immersed and \( m_i \) (initial mass) is the mass of the sample before it is immersed. The wet samples are the samples after they are immersed in DME and DME/LPG mixtures and the dry samples are the samples after they are exposed to room temperature for 24 hours.

2.7. Swelling measurement
Volume swelling of compound after immersion is determine according to the ASTM D 471-16a standard.

3. Results and Discussion

3.1. Curing Characteristic
The curing characteristic of rubber compound can be seen in Table 2. From the table, we can see that compound 6 has the highest torque (\( S_{\max} \)) than other compounds it means that most cross-linking formed in compound 6 which is uses full NBR and conventional vulcanization system. It can be caused that the conventional vulcanization system is more suitable for NBR compound than for NR compound. But NBR compound with efficient vulcanization system (compound 4) not suitable so its cross-linking is lowest which is indicated by the lowest torque (\( S_{\max} \)) than other compounds.

| Materials | Dosage (per hundred rubber, phr) |
|-----------|----------------------------------|
| \( S_{\max}-S_{\min} \)     | 1  | 2  | 3  | 4  | 5  | 6  |
| S\(_{\max}\)             | 2.81| 4.61| 8.54| 1.83| 4.96| 10.41|
| S\(_{\min}\)             | 3.05| 4.91| 8.77| 2.2 | 5.39| 10.77|
| T\(_{90}\)               | 0.24| 0.3 | 0.23| 0.37| 0.43| 0.36 |
| TS\(_{2}\)               | 11.53| 10.05| 7.44| 9.23| 5.51| 5.18 |
| NA                    | 9.2 | 7.28| 4.36| NA | 3.55 | 2.55 |

3.2. Physical Properties
Physical properties of compound before and after ageing at 70 °C for 168h can be seen in Table 3. From the table, we can see that before ageing, compound 1 which using NR with efficient vulcanization system has the highest tensile strength and the lowest hardness than other compounds and compound 4 which using NBR with the same vulcanization system has the highest elongation at break than other compounds. It can be concluded that efficient vulcanization system is more suitable to get the best physical properties not only for NBR compound but also for NR compound. After ageing, we can see that compound 1 has the best properties than other compounds. So, it can conclude that NR compound with efficient vulcanization system more resistant to ageing than NBR compound with the same vulcanization system.

Physical properties of compound could be compared to SNI 7213:2014 [11] standard about rubber hose for LPG stove as reference. We use this standard because the standard of rubber hose for DME stove has not been published. For physical properties before ageing, elongation at break all compounds has fulfill the standard requirement but for tensile strength, only compounds 1, 2 and 6 has fulfill the standard requirement. For physical properties after ageing, almost all compounds fulfill the standard requirements except compound 3 and compound 6 for elongation at break. The result showed that
compound 3 which using NR with conventional vulcanization system and compound 6 which using NBR with same system vulcanization less resistance to ageing than other compounds.

Meanwhile, for tear strength properties, compound 4 has the lowest tear resistance compared to other compounds. This can be caused by the lowest degree of cross-linking formed as shown in the curing characteristics in Table 2. Whereas the compression set properties of compound 4 actually have the best value compared to other compounds. This can be caused by its low degree of cross-linking so that the elasticity is low as a result the compression set value is also low.

Table 3. Physical properties of NBR and NR compounds with the variation of vulcanization system before and after ageing

| Physical Properties | Standard Requirement SNI 7213:2014 | Vulcanized | 1 | 2 | 3 | 4 | 5 | 6 |
|---------------------|-------------------------------------|------------|---|---|---|---|---|---|
| Hardness (Shore A)  | -                                   | -          | 55 | 63 | 68 | 63 | 67 | 73 |
| Tensile strength (MPa) | Min. 7                             | Min. 7    | 15.9 | 12.1 | 5.8 | 5.7 | 6.9 | 7.5 |
| Elongation at break (%) | Min. 200                           | Min. 250  | 500 | 450 | 270 | 1000 | 570 | 310 |

| Change after ageing 70 °C, 168h : |
|-----------------------------------|
| Δ Hardness (Shore A) | Max. 10 | Max. 10 | 5 | 5 | 5 | 3 | 3 | 3 |
| Δ Tensile strength (%) | Max. ± 30 | Max. ± 30 | 3.77 | -27.27 | -25.68 | 0 | -28.99 | -29.33 |
| Δ Elongation at break (%) | Max. -35 | Max. -35 | -6.00 | -17.78 | -62.96 | -13.00 | -28.07 | -67.74 |
| Tear strength (MPa) | - | - | 32.2 | 36.2 | 31.1 | 21.2 | 28 | 25.7 |
| Compression set, temp. 27±2 °C (%) | - | - | 12.78 | 10.11 | 9.21 | 47.71 | 20.88 | 16.59 |

3.3. Effect of immersion

Physical properties of compounds before and after immersion in DME and DME/LPG mixtures can be seen in Table 4. Effect of immersion to compound could be compared to SNI 8758:2019 [12] standard about low-pressure regulator for DME tube as reference. From the table, we can see that all compounds fulfill the standard requirements except compound 4 which can not be measured because its compound has the greatest swelling volume after immersion as can be seen in Figure 2.

Table 4 shows the mass changes (%) for the dry samples. The samples were measured using an analytical balance after the samples were aired for 24 hours at room temperature. As shown in Table 4, the value of the mass change for all of the dry samples is positive. The phenomenon, “like dissolves like”, caused DME to be absorbed into the network of the vulcanized natural rubber samples during immersion [7]. The network in the samples was formed by cross-linking during the vulcanization process [13]. This induces the increase in the percentage change in the mass of the vulcanized rubber. When DME is absorbed in the network of rubber, a reaction occurs between the DME and some of the compounds in the vulcanized rubber, this causes a decrease in the mass.

From Figure 2 we can see that compound 4 which is use full NBR and efficient vulcanization system has the worst resistance to DME and DME/LPG mixtures which the result is accordance with curing characteristic in Table 2. Compound 4 has the worst resistance to DME and DME/LPG mixtures because it’s cross-linking is the lowest than other compounds, which is caused by the compound not cured well. So, when it immersed in DME and DME/LPG mixtures, it becomes swell. Based on the result we can conclude that NBR with efficient vulcanization system not suitable for rubber compound in DME and DME/LPG mixtures.
Table 4. Physical properties after immersion 72h in DME and DME/LPG mixtures based on SNI 8758:2019 standard about low pressure regulator for DME tube.

| No. | Properties (after 24h) | DME/LPG Mixtures | Compounds 1 | Compounds 2 | Compounds 3 | Compounds 4 | Compounds 5 | Compounds 6 | Standard Requirements |
|-----|------------------------|-------------------|-------------|-------------|-------------|-------------|-------------|-------------|----------------------|
| 1.  | Swelling volume         | 10/90             | 6.59        | 6.81        | 6.95        | NA          | 9.21        | 11.11       | < 25%                |
|     |                        | 20/80             | 6.06        | 5.76        | 7.07        | NA          | 8.1         | 8.49        |                      |
|     |                        | 30/70             | 8.68        | 9.03        | 11.47       | NA          | 14.31       | 12.35       |                      |
|     |                        | 100/0             | 1.3         | 2.12        | 4.13        | NA          | 11.64       | 11.54       |                      |
| 2.  | Loss in weight          | 10/90             | 2.32        | 2.46        | 3.02        | 3.94        | 4.83        | 4.89        | < 10%                |
|     |                        | 20/80             | 1.78        | 1.81        | 2.5         | NA          | 3.74        | 2.56        |                      |
|     |                        | 30/70             | 3.45        | 3.41        | 4.54        | NA          | 5.86        | 5.8         |                      |
|     |                        | 100/0             | 0.58        | 0.55        | 1.73        | 1.26        | 5.65        | 5.78        |                      |

Figure 2. Visualization of vulcanized rubber after immersion in DME/LPG 10/90, 20/80, 30/70 and DME 100% (from left to right)

4. Conclusions
From this research, we can conclude that compound 1 which use full NR with efficient vulcanization system has the best physical properties before and after ageing and the best resistance to DME and DME/LPG mixtures. Follow up this research must be done to produce prototype products such as a membrane or other rubber component in the regulator and tube valve which is used for DME in the future.

Acknowledgement
This work was carried out with the financial support of the Center of Excellent of Ministry of Research, Technology and Higher Education of the Republic of Indonesia through The Sinergy Research with Research and Development Centre for Oil and Gas Technology (LEMIGAS).

5. References
[1] Saputra A H, Johan J, Sari T I, Cifriadi A, Maspanger D R and Bismo S 2016 International Journal of Technology 7 (4) pp 616-624
[2] Thomas G, Feng B, Veeraragavan A, Cleary M J and Drinnan N 2014 Fuel Processing Technology 119 pp 286–304
[3] Semelsberger T A, Borup R L and Greene H L 2006 Journal of Power Sources 156(2) pp 497–511
[4] Anggarani R, Wibowo C S, and Rulianto D 2014 Energy Procedia 47 pp 227–234
[5] Saputra A H, Juneva S, Sari T I and Cifriadi A 2018 IOP Conf. Ser.: Mater. Sci. Eng. 345 012035
[6] Coran A Y 2013 Vulcanization in The Science and Technology of Rubber (Academic Press) pp 337-381
[7] Wu N, Zhang W, and Huang Z 2008 *Frontiers of Energy and Power Engineering in China* 2(3) pp 279–284
[8] Li G B and Zhou L B 2008 *Journal of Automobile Engineering* 222(6) pp 975–978
[9] Trakampruk W and Porntangjitlikit S 2008 *Renewable Energy* 33(7) pp 1558–1563
[10] Abu-Abdeen M and Elamer I 2010 *Materials & Design* 31(2) pp 808–815
[11] SNI 7213:2014 about “Selang Karet untuk Kompor Gas LPG”
[12] SNI 8758:2019 about “Regulator Tekanan Rendah untuk Tabung Baja DME”
[13] Mark J E, Erman B and Roland C M 2013 *The Science and Technology of Rubber Fourth Edition* (Boston: Academic Press)