The effect of natural rubber on physical and mechanical properties of rubber seal for LPG tube valve

H Handayani*, A Ramadhan, A Cifriadi, N A Kinasih, A F Falaah and D R Maspanger
Indonesian Rubber Research Institute, Salak Street No. 1, Bogor, 16128, Indonesia
Email: hani.handayani@puslitkaret.co.id

Abstract. The price of natural rubber (NR) continues to decline. In early January 2020 the price of Standard Indonesian Rubber (SIR) 20 was around 1.83 US$/kg and in May 2020 dropped to 1.09 US$/kg. Under this condition, NR downstream program becomes a necessity to increase domestic consumption of NR so that the sustainable rubber industry can be achieved. One prospective product and can be substituted using NR is the rubber seal for Liquified Petroleum Gas (LPG) tube valve. Based on the rubber seal quality requirements in Standar Nasional Indonesia (SNI) 7655: 2010, the rubber raw material should use rubber which is resistant to n-pentane. Nitrile Butadiene Rubber (NBR) synthetic rubber is suitable, meanwhile NR is not resistant to n-pentane so it is not suitable to produce rubber seal for LPG tube valve. Hence, this research studied the effect of NR on physical and mechanical properties of rubber seal compared to NBR compound. The results showed that NR improved elastic properties such as tensile strength, elongation at break and compression set, but decreased the resistance to n-pentane. Mixing NBR and NR with appropriate compositions can produce a better rubber seal for LPG tube valve.

1. Introduction
Liquified Petroleum Gas (LPG) tube valve must be equipped with rubber seal to prevent gas leakage during usage or gas filling and to strengthen the regulator position. The product quality of the rubber seal in Indonesia must meet the national standard of SNI 7655:2010. This standard has been enforced compulsory referring to the Indonesian Ministry of Industry regulation No: 67 / M-IND / PER / 6/2012.

Rubber seal product quality requires raw material which is resistant to n-pentane according to SNI 7655: 2010. One kind of rubber that is resistant to n-pentane is Nitrile Butadiene Rubber (NBR) which is imported from abroad with the price in the domestic market of 3.50-5.00 USD/kg. The presence of nitrile groups in NBR structure makes it polar rubber so that it is more resistant to non-polar solvents and oils, while it has low mechanical and dynamical properties [1,2,3]. Natural rubber (NR) has excellent mechanical and dynamical properties [4], but it has low chemical resistance [5]. As a result, it cannot be used for making rubber seal of LPG tube valve. To increase the resistance of natural rubber to oil or gas, modification is required. Modification of natural rubber is needed to enhance the mechanical properties of NBR, to improve NR resistance to n-pentane, and primarily to increase domestic consumption of NR.

Modification of natural rubber can be done both chemically and physically. Chemical modification is done through an epoxidation reaction to produce oil-resistant natural rubber that is called epoxidized natural rubber, but it requires a relatively high cost [6]. Meanwhile, physical modification is done
through mixing (blending) natural rubber with synthetic rubber NBR [7,8,9], and it requires lower costs than using modified natural rubber. Thus, this method was chosen to make formulas of rubber seal compounds.

A study on vulcanized rubber of NR/NBR mixtures (41% acrylonitrile) in different compositions with variations in the amount of carbon black has been done by [10]. The results showed that the compositions of the NR/NBR mixtures (40/60, 60/40 and 80/20) had a modulus of 100% which were greater than the modulus of 100% NR and NBR. Meanwhile, the tensile strength decreased with more NBR content in the mixture. The tensile strength of the mixtures was smaller than NR and NBR especially at low hardness. This indicated that NR and NBR were not compatible each other. The compression set of the NR/NBR mixtures increased with the smaller NR content in the mixtures. Compression continued to improve with the increased hardness of vulcanized rubber. The best compression sets were obtained from the compositions of 20/80 and 40/60 NR/NBR mixtures. The swelling properties using ASTM oil no.3 showed that the composition of the 20/80 NR/NBR mixture was best followed by the 40/60 composition. Baker concluded that NBR (41% acrylonitrile) could be substituted with a mixture of 20/80 NR/NBR.

Another study that investigated the properties of NR/NBR mixture without fillers by using dicumyl peroxide as a vulcanizing agent has been conducted by [11]. The result showed that the tensile strength trend with varied NR/NBR mixture compositions was different from those shown by [10]. The swelling properties were getting better with more NBR in the mixtures.

Several studies also have shown that the NR/NBR mixture with compatibilizer or homogenizer could increase the mechanical properties [8,12] and the swelling behavior in ASTM oil No. 1 and No. 2 [9,13], toluene [13]. Mixing natural rubber with NBR rubber can be done by using solvents, by mechanical or using rubber powder. The most common method used in the industry is by mechanical in the banbury or open mill. In this research, the natural rubber was mixed with NBR in an open mill. However, there was little information about the effect of natural rubber on physical and mechanical properties of rubber seal for LPG tube valve. Therefore, this study aims to study the effect of natural rubber on physical and mechanical properties of rubber seal compounds, such as hardness, tensile strength, elongation at break, compression set, swelling properties and resistance to ozone.

2. Materials and Methods

2.1. Materials

The materials used in this study include Natural Rubber (NR), Standard Indonesia Rubber (SIR) 20 obtained from local suppliers, Nitrile Butadiene Rubber (NBR) Krynan 3345 from Arlanxeo, and technical quality of rubber compounding chemicals from local suppliers. The rubber compounding chemicals include: sulfur as the vulcanization agent, stearic acid and zinc oxide as the activator, Si-69 (bis-triethoxy silyl propyl-tetrasulfide) as the coupling agent, red pigment as the color pigment, silica zeosil 175 MP as the filler, PEG (polyethylene glycol) as the dispersing agent, Antilux 654A as the antiozonant, MMB (mercaptoethyl benzimidazole) and TMQ (trimethyl dihydroquinoline) as the antioxidant, DOP (dioctyl phthalate) as the plasticizer for NBR, paraffinic oil as the plasticizer for NR, CBS (cyclohexyl benzoathiazole sulfenamide) and TMTD (tetramethyl thiuram disulfide) as the accelerator, and lastly PVI (N-cyclohexylthio phthalimide) as the retardant.

2.2. Rubber seal compounding

Natural rubber and NBR were blended with other ingredients in the two-roll open mill according to the compound formulas. The addition of chemicals used a unit of phr (per hundred rubbers). This was used for calculating formulas where other chemicals were calculated as parts per 100 weight of rubber. Compounds were formulated with variations in 5 types of elastomer as seen in table 1. The compounds were then cured in a press machine at 150 °C to form the vulcanized rubber. The physical properties were then tested for hardness, tensile strength, elongation at break, and compression set at room temperature.
Table 1. The compounding formulas with various kinds of elastomer.

| Compounding ingredients | Compound B (10% NR) | Compound C (20% NR) | Compound D (30% NR) | Compound E (100% NR) |
|-------------------------|---------------------|---------------------|---------------------|-----------------------|
| NBR 3345                | 100                 | 90                  | 80                  | 70                    |
| NR                      | -                   | 10                  | 20                  | 30                    |
| Silica 175 MP           | 40                  | 40                  | 40                  | 40                    |
| Silane Si-69            | 2                   | 2                   | 2                   | 2                     |
| PEG                     | 2                   | 2                   | 2                   | 2                     |
| Color pigment           | 1                   | 1                   | 1                   | 2                     |
| Antilux 654A            | 3.5                 | 3.5                 | 3.5                 | 3.5                   |
| MMB                     | 2                   | 2                   | 2                   | 2                     |
| TMQ                     | 1.5                 | 1.5                 | 1.5                 | 1.5                   |
| Paraffinic oil          | -                   | -                   | -                   | 8                     |
| DOP                     | 8                   | 8                   | 8                   | -                     |
| Zinc Oxide              | 2                   | 2                   | 2                   | 2                     |
| Stearic Acid            | 0.5                 | 0.5                 | 0.5                 | 0.5                   |
| CBS                     | 2.4                 | 2.4                 | 2.4                 | 2.4                   |
| TMTD                    | 3                   | 3                   | 3                   | 3                     |
| PVI                     | 0.5                 | 0.5                 | 0.5                 | 0.5                   |
| Sulphur                 | 0.4                 | 0.4                 | 0.4                 | 0.4                   |

2.3. Curing characteristics
Before curing, the mixtures of natural rubber and NBR were tested for the curing characteristics using MDR 2000 rheometer. The rheometer test was aimed at obtaining optimum vulcanization time and other maturation characteristics, such as maximum torque, minimum torque and scorch time.

2.4. Physical and mechanical testing
The vulcanized rubber was prepared in the form of test samples on the basis of standard methods. To test the hardness, the standard method was based on ASTM D 2240-15. Besides, the standard method for testing the tensile was based on ASTM D 412-16 and for elongation at break was based on SNI ISO 37:2015. The standard method for testing the compression set was according to ISO 815-1:2014 and for testing the swelling volume in n-pentane was according to ISO 1817:2015. The results of these physical properties were compared to the physical properties of rubber seal of LPG tube valve in SNI 7655:2010 [14].

3. Results and discussion

3.1. Curing characteristics
The curing characteristics, expressed in terms of maximum torque (S’ max) value, minimum torque (S’ min) value, delta torque (∆S’ = S’ max – S’ min), optimum cure time (t90) and scorch time (ts2) of rubber compounds are shown in table 2. From the table, it can be seen that the compounds which used natural rubber at minimum 20% NR (compounds C, D and E) obtained higher maximum torque and delta torque values than full NBR compound (compound A). It means that more cross-linking was formed in the compounds using minimum 20% NR. Besides that, all compounds with natural rubber got lower optimum cure time and scorch time than that of full NBR compound, meaning that the compounds which used NR cured faster than full NBR compound. Faster cure or vulcanization time is needed by the industry to reduce cost production. From this curing characteristics aspect, it can be
concluded that the substitution of minimum 20% NBR by natural rubber is better in NBR-NR compounding formulation.

### Table 2. Curing characteristics of rubber seal compounds with variations in elastomer.

| Curing Characteristics | Compounding Formulation |
|------------------------|--------------------------|
|                       | A (0% NR) | B (10% NR) | C (20% NR) | D (30% NR) | E (100% NR) |
| ΔS’ (Kg-cm)            | 20.15     | 17.42      | 22.76      | 21.56      | 21.91      |
| S’\text{max} (Kg-cm)   | 21.36     | 18.88      | 24.64      | 23.29      | 23.13      |
| S’\text{min} (Kg-cm)   | 1.21      | 1.46       | 1.88       | 1.73       | 1.22       |
| T\text{90} (min)       | 18.23     | 15.08      | 16.24      | 17.59      | 15.34      |
| TS\text{2} (min)       | 4.08      | 3.22       | 2.26       | 3.28       | 2.34       |

3.2. Physical and mechanical properties

The physical and mechanical properties of rubber seal compounds for LPG tube valve can be seen in Table 3. It shows that the hardness of compounds A-E were slightly greater than the requirement of SNI 7655: 2010. This might be caused by the excessive amount of filler added which increased the hardness. In order to reduce the hardness value to fulfill the standard requirement, either the filler dose has to be reduced or the plasticizer dose has to be increased. On the other hand, the values of elasticity such as tensile strength and elongation at break of all compounds fulfilled the standard requirements. This was because of the use of natural rubber in the compounds that improved the elasticity. Besides that, the values for resistance of ozone obtained from all the compounds also could meet the standard requirements. At the same time, the values of swelling properties in n-pentane from compounds A-D met the standard requirements, while compound E which used 100% natural rubber was not resistant to n-pentane because of the polarity of natural rubber. Furthermore, the compression set values from all of the compounds did not meet the standard requirements. Thus, reformulation is still required to improve the compression set properties of the rubber seal for LPG tube valve.

### Table 3. Physical properties of rubber seal compounds with variations in elastomer.

| Physical Properties                        | SNI 7655:2010 Requirement | Compounding Formulation |
|-------------------------------------------|---------------------------|-------------------------|
|                                           | A (0% NR) | B (10% NR) | C (20% NR) | D (30% NR) | E (100% NR) |
| Hardness (Shore A)                        | 60 ± 5     | 67         | 67         | 67         | 67          | 68          |
| Tensile strength (MPa)                    | Min. 10    | 12.6       | 12.6       | 13.5       | 14.0        | 23.4        |
| Elongation at break (%)                   | Min. 300   | 340        | 350        | 400        | 420         | 610         |
| Compression set, temp. 27±2 °C (%)        | Max. 10    | 12.77      | 11.43      | 11.51      | 11.21       | 10.19       |
| Swelling volume in n-pentane at RT, 168 h | Max. +35   | 13.24      | 20.29      | 22.21      | 31.64       | 69.74       |
| Swelling volume in n-pentane at 70 °C, 96 h| Max. -12   | -4.30      | -7.6       | -7.61      | -8.34       | -3.26       |
| Resistance to ozone                       | No crack   | No crack   | No crack   | No crack   | No crack    | No crack    |
4. Conclusion
From this research, it can be concluded that the use of natural rubber as the substitution of NBR in rubber seal compounds improved the elasticity properties of the rubber seal for LPG tube valve. The usage of minimum 20% NR showed better curing characteristics than that of the full NBR compound. Meanwhile, in terms of physical and mechanical properties, the use of 30% natural rubber resulted in the best properties and meet most of the requirements of SNI 7655: 2010, except for the compression set. In conclusion, the natural rubber as the substitution for NBR in making the rubber seal for LPG tube valve can be used at a range of 20%-30%, but reformulation is still necessary to improve the compression set properties.

Acknowledgments
This work was carried out with the financial support of the Indonesia Endowment Fund for Education or Lembaga Pengelola Dana Pendidikan (LPDP), Ministry of Finance of the Republic of Indonesia through the Productive and Innovative Research or Riset Inovatif Produktif (RISPRO) grant with the contract number 57/LPDP/2019. Hani Handayani, Arief Ramadhan and Adi Cifriadi as the main contributors of this paper are also thankful to the other members as their co-authors.

References
[1] Thabet A M, Abouel-Kasim A, Bayoumi M R and El-Sebaie M G 2009 Effect of carbon black loading in the swelling and compression set behaviour of SBR and NBR rubber compounds Mater. Design 30(5) 1561-68
[2] Wang H M, Lu X R and Wang S J 2014 The swelling properties of nitrile rubber with different acrylonitrile contents in cyclohexane medium research Adv. Mat. Res. 936 1942-47
[3] Choi S S and Ho H S 2009 Influence of the swelling temperature and acrylonitrile content of NBR on the water swelling behaviors of silica-filled NBR vulcanizates J. Ind. Eng. Chem. 15(2) 167-70
[4] Ismail H, Majid R A and Taib R M 2014 Effects of dynamic vulcanization on tensile, morphological, and swelling properties of poly(vinyl chloride) (PVC)/ epoxidized natural rubber (ENR)/(Kenaf core powder) composites J. Vinyl Addit. Techn. 22(3) 1-7
[5] Yasin K A, Ansarifar A, Hameed S and Wang L 2011 A new method for crosslinking and reinforcing acrylonitrile-butadiene rubber using a silanized silica nanofiller Polym. Adv. Technol. 22(2) 215-24
[6] Gelling I R 1991 Epoxised natural rubber J. Nat. Rubb. Res. 6(3) 184-205
[7] Lewan M V 1998 NR/NBR blends – basic problems and solutions in blend of natural rubber (London: Chapman & Hall)
[8] Kongsin K and Lewan M V 1998 Improving the morphology and properties of NR/NBR blends with polychloroprene as the compatibilizing agent in blend of natural rubber (London: Chapman & Hall)
[9] Karnika de Silva, K G and Lewan M V 1998 Improving phase morphology and properties of NR/NBR blends with compatibilizer J. Rubb. Res. Institute of Sri Lanka 81 38-50
[10] Baker C, Hallam W G and Smith, I F 1974 NR Tech. 5(2) 29
[11] Ahmad M and Wheelans M A 1984 NR Tech. 15(4) 78
[12] Go J H and Ha C S 1996 Rheology and properties of EPDM/BR blends with or without a homogenizing agent or a coupling agent J. Appl. Polym. Sci. 62(3) 509-21
[13] Edirisinghe D and Freakley P K 2003 Effect of varied carbon black distribution on the morphology and properties of blends of natural and nitrile rubber J. Rubb. Res. Institute of Sri Lanka 86 58-79
[14] Standar Nasional Indonesia (SNI) 7655:2010 about Rubber seal of LPG Tube Valve (Jakarta: Badan Standardisasi Nasional (BSN))