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Effect of Organomodified Bentonite/Silica Hybrid Filler Compound System on Mechanical Properties and Sealing Performance of NR/NBR Rubber Seal for LPG Tube Valve

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Organomodified bentonite and silica were used as hybrid fillers in natural rubber (NR)/nitrile butadiene rubber (NBR) seal for liquified petroleum gas (LPG) tube valve compound to evaluate their interaction and influence on mechanical properties and sealing performance. In this work, the NR-organomodified bentonite were prepared by the *in situ* organomodified and latex compounding method with varying amounts of bentonite then applied in the silica-NR/NBR rubber seal compounds with mixing process held in two rolls open mill. Silanization reaction, Payne effect, curing characteristics, tensile properties, compression set, hardness, uniaxial compression and sealing performance were assessed. The study obtained that NR/NBR-silica/organomodified bentonite show improved silica dispersion physically, as analyzed by Payne effect. The presence of organomodified bentonite decreases the vulcanization reaction. The cure rate index, apparent crosslink density and hardness tend to decrease with addition of organomodified bentonite, while tensile strength and elongation at break are enhanced with increasing organomodified bentonite. With an appropriate amount of organomodified bentonite (organomodified bentonite below 4 phr), the introduction of organomodified bentonite enhances the elastic response of the material, as shown by increasing of tensile properties. The rubber seal's sealing performance analysis revealed that B4 (4 phr organomodified bentonite) performed the best, with contact stress higher than the actual working pressure and Misses stress lower than the actual working pressure, making it difficult to crack.

Keywords: Rubber seal, Hybrid filler, Natural rubber, Organomodified bentonite, Sealing performance.

INTRODUCTION

Since Government of Indonesia launched the conversion program of kerosene to liquified petroleum gas (LPG) from 2007, Pertamina has a mandate to carry out the supply and distribution of LPG. This program was success to increased percentage of households using LPG from 6.4% in 2007 became 91.1% in 2013 [1]. However, this program has several problems such as leakage and explosion of LPG tubes [2]. Rubber seal was assembled in the liquified petroleum gas (LPG) tube valve as protector to avoid the gas leakage during gas filling or tube using and to strengthen the regulator position. The safety parameter is the important key factor to be concern in the usage of LPG tube. The design of rubber seal compound must be meet the national rubber seal requirement (SNI 7655:2010) in mechanical properties and dimensional stability aspect, but still has minimum cost production [3].

Blending of natural rubber (NR) and nitrile butadiene rubber (NBR) is one way of the design of rubber seal compound, because rubber seal product need NBR as raw material, which is resistant to *n*-pentane as non-polar solvent [4], representative of LPG, according to SNI 7655:2010, meanwhile NR has better mechanical and dynamical properties and cheaper than NBR [5,6]. Decision from Pertamina to change rubber seal colour from black to red also affects the design of rubber compound, because it need silica as reinforcing filler to change carbon black as widely used for reinforcing filler in black rubber compound. Silica has been used to replace carbon black as reinforcing agent, however the presence of polar silanol groups on the surface of silica result in strong filler-filler interaction by hydrogen bonds, make it incompatible with non-polar rubber including NR, thus resulting poor dispersibility of silica in the NR matrix. Silica-filled rubber compound also delay the scorch and cure times, because adsorption of accelerator by silica [7].

Various silane coupling agents and compatibilizers have been used in silica-filled rubber compounds to solve this problem, such as TESPT, NXT, TEOS, Si69 [7-10] could be use as silane coupling agents. A silane coupling agent has organofunctional group which react with the rubber and hydrolyzable alkoxy groups, which react with the silanol groups on the silica surface, known as silanization reaction, which can improve silica dispersion and increase the adhesion between rubber and silica. Meanwhile, NBR can act as compatibilizers on silica filled NR compound, because nitrile group in NBR could make a hydrogen bond with the silanol group of silica leading to strong NBR-silica interaction. Silica dispersion and mechanical properties of the silica filled NR composite were found to be improved significantly [8].

Another approach to enhance dispersibility of silica in NR matrix is by using hybrid or dual filler. Organomodified clay, organoclay (OC) or organomodified bentonite was added to silica based elastomeric composite to form hybrid filler system led to reduction of filler-filer interaction or filler network of silica [11]. Many studies in the scientific literature have reported the hybrid system of organoclay-silica in various rubber matrixes, *e.g.* NR [7], SBR-BR [10], Polyisoprene [11], SBR-NBR [12] and silicone rubber [13]. Meanwhile organoclay was also studied as single filler in NR/NBR matrix, exhibit high tensile strength and modulus value [14,15].

Further studies illustrating the synergy of silica and organoclay hybrid fillers in NR/NBR composites are scarce. In present work, an attempt is made to study the mechanical properties and sealing performance of NR/NBR composites reinforced with silica-organomodified bentonite, used as rubber seal product for LPG tube valve.

EXPERIMENTAL

For the preparation of natural rubber (NR)-organomodified bentonite masterbatch, high-ammonia concentrated NR latex with dry rubber content of 60% was purchased from local supplier in Indonesia. Organomodified bentonite with a cation exchange capacity of 72.82 meq/100 g was purchased from local supplier in Indonesia. Dihydrogenated tallowylethyl hydroxyethylmonium methosulfate (Tetranyl AT-7590) cationic surfactant with a melting point of 40 ºC and polyoxyethylene lauryl ether (Emulgen 147) non-ionic surfactant was supplied by Kao Corporation (Indonesia). For the rubber compound preparation, the NR used was Standard Indonesian Rubber (SIR 20), locally produced in Indonesia. The NBR of Krynac 3345 with acrylonitrile content 33% was supplied from PT. Multi Citra (Indonesia). The compounding ingredients were silica with a specific surface area of 175 m^2/g (Zeosil 175 MP, Solvay, China), *bis*-(3-triethoxysilylpropyl) tetrasulfide (TESPT; JH-S69, Jianghan Fine Chemical Co. Ltd., China) and Rhenosin 260 from Lanxess. Other chemicals including *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), polyethylene glycol (PEG), DOP (dioctyl phthalate), 2-mercapto-4(or 5)-methyl benzimidazole (MMB), tetramethyl thiuram disulfide (TMTD), 4,4′-dithiodimorpholine (DTDM), zinc oxide, stearic acid, PVI and sulphur were commercial-grade products for rubber compounding.

Preparation of NR-organomodified bentonite masterbatch: The NR-organomodified bentonite masterbatches containing 15 phr of bentonite, 3 phr of non-ionic surfactant and 8.6 phr of cationic surfactant were prepared by using *in situ* organomodified and latex compounding method [16]. Three phr non-ionic surfactant (Emulgen 147) was used to stabilize diluted high ammonia concentrated NR latex with 40% dry rubber content. Ammonia was evaporated for 4 h prior to being left overnight at room temperature. Thereafter, 8.6 phr of cationic surfactant (Tetranyl AT-7590) were added into stabilized NR latex and mechanically stirred at 300 rpm for 15 min. Meanwhile, the dispersion of bentonite was prepared by stirring 15 g of bentonite and 735 mL of hot distilled water (65 ºC) at 300 rpm and the homogenizing 2500 rpm for 15 min. After that NR latex containing non-ionic and cationic surfactant was subsequently mixed with 2% bentonite dispersion at 600 rpm for 30 min and then coagulated using methanol, wash with water flow and dried in an oven at 60 ºC until constant weight.

Preparation of rubber seal compounds: Rubber seal compounds were prepared using the formulations as tabulated in Table-1. The pure NR/NBR compound without NR-organomodified bentonite masterbatch was prepared as control by using 35 phr of silica. For NR/NBR-silica/organomodified bentonite compounds, the compounds containing different amount of organomodified bentonite (0, 2, 4, 6 phr), are coded as B0, B2, B4, B6. The NR-organomodified bentonite masterbatch which originally contained 15 phr of organomodified bentonite was mixed with NR (SIR20) in a proportion that would result in a final compound having 2, 4 and 6 phr of organomodified bentonite. The mixing was carried out using two roll mill at 65 ± 5 ºC. Natural rubber (SIR 20) and NR-organomodified bentonite masterbatch was masticated for 5 min and then mixed with NBR, after that, another ingredients was added into two roll mill except accelerator, PVI and sulfur. The compound without accelerator and vulcanizing agent (unvulcanized compound) was take for study the silanization reaction and characterized.

TABLE-1
COMPOUND FORMULATION

Material	B0	B2	B4	B6
NBR 3345	60	60	60	60
SIR 20	40	26.67	13.33	0
NR/organomodified bentonite masterbatch	0	16.86	33.72	50.58
Rhenosin 260	5	5	5	5
Zeosil 175 MP	35	35	35	35
TESPT	2	2	2	2
PEG	2	2	2	2
Colour pigmen	1	1	1	1
White factice	5	5	5	5
Antilux	2	2	2	2
MMB	2	2	2	2
DOP	15	15	15	15
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
CBS	4.5	4.5	4.5	4.5
TMTD	2	2	2	2
DTDM	3	3	3	3
PVI	1.5	1.5	1.5	1.5
Sulphur	0.3	0.3	0.3	0.3

Silanization reaction of NR/NBR-silica/organomodified bentonite unvulcanized compound and bound rubber measurement: To study the effect of organomodified bentonite on the silanization reaction, NR/NBR-silica/organomodified bentonite unvulcanized compound containing different amount of organomodified bentonite (0, 2, 4 and 6 phr) was pressed using Moving Die Rheometer at 150 ºC for 10 min (MDR, Alpha, USA). Similar silanization reaction condition was prepared using brabender [17]. Thereafter, the bound rubber of NR/NBR-silica/organomodified bentonite unvulcanized compound was determined with and without ammonia treatment.

Bound rubber contents were characterized both with and without ammonia treatment. The ammonia treatment was done to determine chemically bound rubber content [7]. The NR/NBR-silica/organomodified bentonite unvulcanized compound (0.2 g) was cut into small pieces, put into a metal cage and then immersed in toluene in either a normal or an ammonia atmosphere for 7 days. Then, the samples were dried at 105 ºC for 24 h. The weights of the samples before and after extraction were measured and the bound rubber contents were calculated by eqn. 3 [18].

$$\text{Bound rubber content (\%)} = \frac{m - m_s}{m_r} \times 100 \qquad (1)$$

where m is the weight of sample after extraction, m_s is the weight of filler in the sample and m_r is the weight of rubber in the sample.

Payne effect of NR/NBR-silica/organomodified bentonite unvulcanized compounds: The Payne effect of unvulcanized compounds was investigated using Rubber Processing Analyzer (RPA, Elite, TA Instrument, USA). The unvulcanized compound was heated at 150 ºC for 10 min and then the change of storage modulus (G′) with strain was characterized by RPA at 100 ºC, a frequency of 0.5 Hz under varying strains from 0.1 to 100%. The Payne effect was determined from the first sweep G′ at low and high strain, *i.e.* at 1% and 100%, respectively.

Characterization of rubber seal compounds

Curing characteristics: After mixing in two roll open mill, the rubber compound stored and left for over night before curing. Certain amount of compound sample was tested in Moving Die Rheometer (MDR, Alpha, USA) at 150 ºC at an oscillation frequency of 1.67 Hz and strain amplitude of 0.5º to determine the curing characteristics, *i.e.* minimum torque (ML), maximum torque (M_H), scorch time (t_1) and optimum curing time (t_{90}).

Tensile properties: Vulcanized sheets of about 2 mm thickness were prepared by pressing NR/NBR-silica/organomodified bentonite compound using press machine at 150 ºC and 100 kg/cm^2. Thereafter, die was cut to dumbbell type 2A specimens and tested by a universal testing machine (MTS Exceed E43, USA) at a crosshead speed of 500 mm/min at room temperature according to ISO 37. Five specimens were tested for each sample and the median value is reported.

Compression set: The specimen (cylinder with diameter of 13 mm and height of 6.0 ± 0.2 mm) is compressed to 75% of its original thickness. The test assembly is then conditioned for the specified time at the selected test temperature after which the specimens are removed and allowed to recover at room temperature for 30 min. Compression set is the difference between the original thickness of the specimen and the thickness after testing, as a percentage of the deflection employed.

Hardness: The hardness was determined by using a Shore A durometer following ASTM D2240-15.

Uniaxial compression: NR/NBR-silica/organomodified bentonite vulcanizates with 29 mm diameter and 12 mm height were compressed using universal testing machine (MTS Exceed E43, USA) at a crosshead speed 10 mm/min at room temperature until a strain of 50% was reached according to ISO 7743. The force-deformation curve was recorded.

Sealing performance of rubber seal compounds: The sealing performance of rubber seal of LPG tube valve is not only related to the contact stress among rubber seal and regulator but also related to the dimension of tube valve. By considering this, some workers support the use of sealing performance coefficient (K) to evaluate the sealing performance of rubber seal of LPG tube valve [19]. The sealing performance coefficient (K) is equal to the product of the effective contact stress among rubber seal, tube valve and regulator, as well as their effective contact length, as shown in eqn. 2 [14]:

$$K = C_P \times C_L \qquad (2)$$

where C_P is effective contact stress and C_L is effective contact length.

The sealing performance was determined using Finite Element Analysis. The uniaxial tension and compression data were fitted by least square method and the numerical simulation was performed by finite element analysis.

RESULTS AND DISCUSSION

Silanization reaction of NR/NBR-silica/organomodified bentonite unvulcanized compound and bound rubber measurement: The silanization reaction of NR/NBR-silica/organomodified bentonite was characterized using MDR in order to investigate the effect of organomodified bentonite loading on silanization reaction. The results of the silanization reaction between NR/NBR and silica/organomodified bentonite are shown in Fig. 1. It was observed that the addition of organomodified bentonite below 2 phr sharply reduces the torque to the minimum torque and after that it increases slowly with the addition of more organomodified bentonite and becomes constant with the addition of organomodified bentonite above 6 phr. In the presence of non-ionic and cationic surfactant in the NR/organomodified bentonite masterbatch act as plasticizer result in decreasing torque minimum.

Torque of unvulcanized NR/NBR-silica with and without organomodified bentonite increase with increasing time, indicating that the silanization reaction occurred in the system. Supposedly a strong silica-elastomer interaction on NR/NBR-silica/organomodified bentonite is obtained through chemical bonding with the formation of a silane bridge. The slope of curve indicates the rate of silanization reaction in unvulcanized NR/NBR-silica with and without organomodified bentonite.

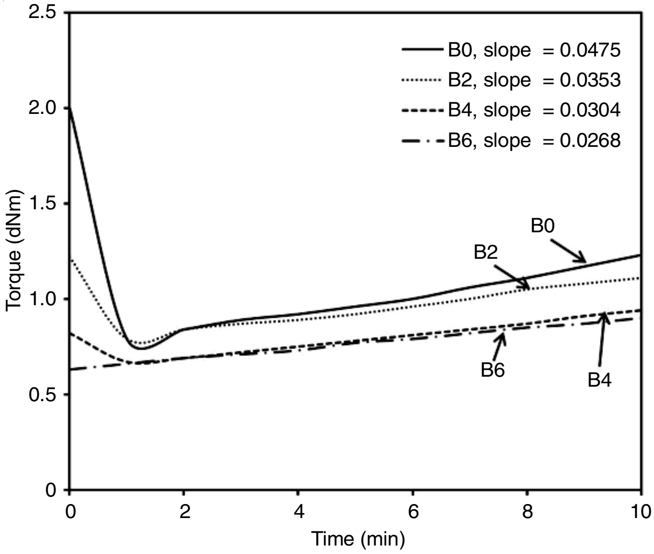

Fig. 1. Effect of organomodified bentonite on the silanization reaction

It is clear that the slope decrease with increasing organomodified bentonite content in NR/NBR-silica. From these results, it can be concluded that the addition of organomodified bentonite into NR/NBR-silica inhibit the silanization reaction in the NR/NBR-silica/organomodified bentonite. A decrease value in slope indicates the decreasing chemical interaction between silica and NR/NBR.

Filler-rubber interaction of silica-filled compound form bound rubber that involves chemical and physical adsorption [7]. The total bound rubber was determined by extracting unbound rubber chains and organic additives from the filled rubber compound with toluene at a normal atmosphere, whereas the chemically bound rubber contents was measured after applying ammonia treatment to cleavage the physical linkages that are formed by physical adsorption. Fig. 2 shows physically and chemically bound rubber contents (PBR = physically bound rubber and CBR = chemically bound rubber) of NR-silica/organomodified bentonite with and without organomodified bentonite as control. It is observed that the addition of organomodified bentonite up to 4 phr decrease the chemical adsorption and increase the physical adsorption of organomodified bentonite into NR/NBR-silica matrix.

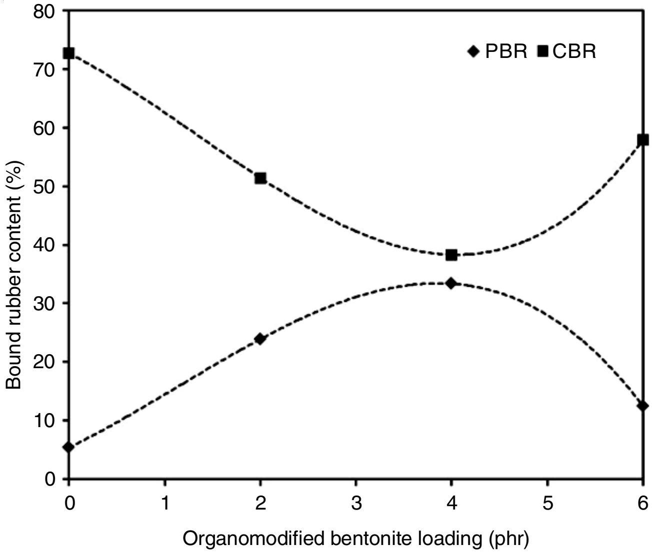

Fig. 2. Bound rubber of NR/NBR-silica/organomodified bentonite unvulcanized compound

Different result was shown for NR-silica/montmorillonite, the presence of organomontmorillonite increased chemical bound rubber and decreased physical bound rubber [7]. The silanization reaction occurred in the internal mixer using high shear mixing and high temperature. In this work, the preparation of rubber compound using open mill at temperature around 60-70 °C. The silanization was presumed occurred during pressing of rubber compound. Therefore, it was presumed that the surfactant may interact with silica, amine compound in the surfactant interact with silanol group on the silica surfaces, without the heating in the open mill this interaction with organomodified bentonite only physical interaction.

Payne effect of NR/NBR-silica/unvulcanized compounds: The strain sweep analysis of NR/NBR-silica with and without organomodified bentonite unvulcanized compound was performed using RPA. The filler-filler interaction commonly called Payne effect, which was determined using the changing in storage modulus at high strain and low strain. Fig. 3 shows the strain dependence of G′ at 100 °C of NR/NBR-silica with and without organomodified bentonite. The Payne effect of NR/NBR-silica without organomodified bentonite is higher than that of NR/NBR-silica/organomodified bentonite. The results indicate that organomodified bentonite layers dispersed well in NR/NBR matrix and reduce filler-filler interaction of silica. The organomodified bentonite layers were dispersed between silica and in the presence of surfactant on the organomodified bentonite surfaces provide the surface shielding on silica [7].

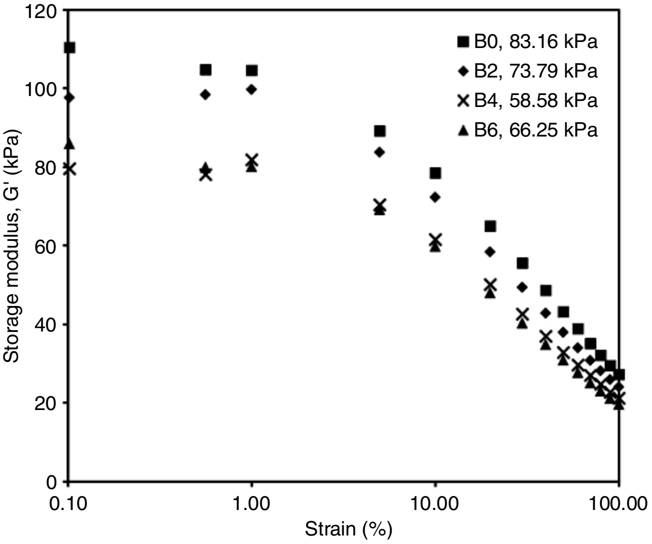

Fig. 3. Payne effect of NR/NBR-silica/organomodified bentonite unvulcanized compound

Characterization of rubber seal compounds: Fig. 4 shows the cure characteristic of rubber seal compounds with and without organomodified bentonite in terms of scorch time (t_2), optimum cure time (t_{90}), cure rate index, minimum torque

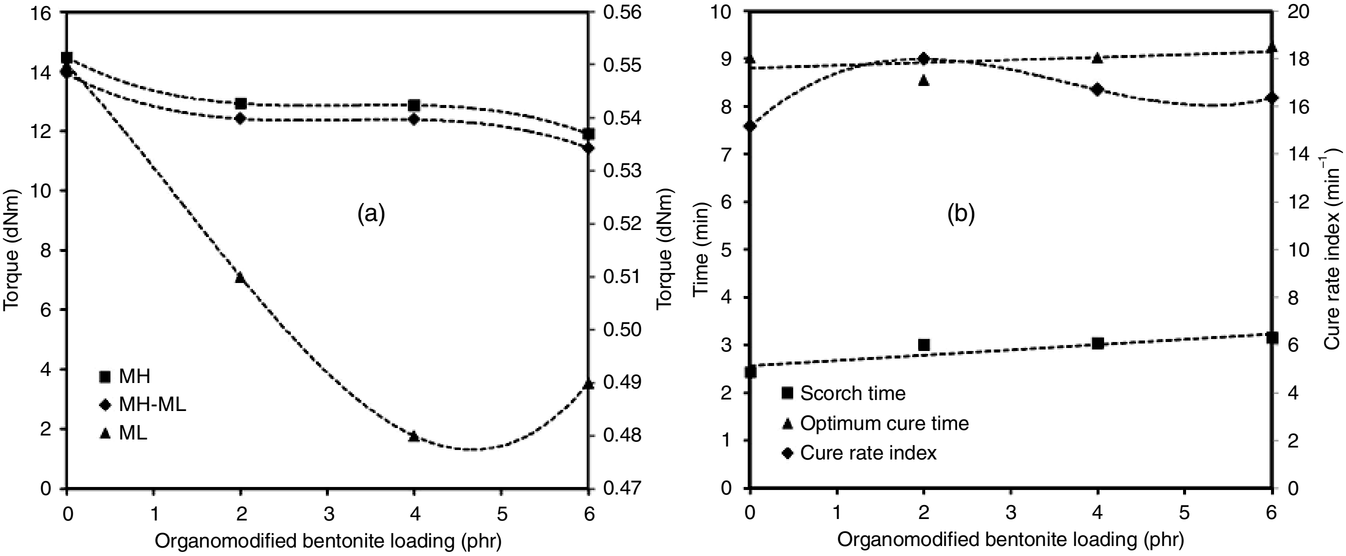

Fig. 4. (a) Cure torque and (b) scorch time, optimum cure time and cure rate index of NR/NBR rubber seal compound

(ML), maximum torque (M_H), as well as torque difference (M_H-ML). The addition of organomodified bentonite slightly decrease the maximum torque and torque difference and sharply decreased the minimum torque up to 4 phr. The minimum torque is related to viscosity of the rubber compound, the decreasing of minimum torque indicates better processing of the rubber compounds. In addition, the minimum torque of the rubber seal compound containing 6 phr of organomodified bentonite slightly increased due to the increasing of chemical bound rubber as shown in Fig. 4.

The addition of organomodified bentonite into rubber seal compounds slightly increase the scorch time (t_2) and optimum cure time (t_{90}), while the cure rate index shows irregular pattern. The retardation effect of the vulcanization process can be caused by the excess of fatty acid within the surfactant, which reduce the crosslinking reaction and decrease the crosslink density [20].

The tensile curve and tensile properties of the rubber seal compound with and without organomodified bentonite are shown in Fig. 5. The tensile curve (Fig. 5a) shows that the addition of organomodified bentonite sharply increases the stress as the strain increases. The addition of organomodified bentonite to the rubber seal compound decreases the modulus at higher strain (> 50%) due to the plasticizing effect of cationic surfactant. However, the tensile strength of rubber seal vulcanizates enhance with increasing organomodified bentonite content. The increasing of tensile strength and elongation at break due to the better interfacial interaction between rubber and filler [21].

The effect of addition of organomodified bentonite to compression set and hardness of rubber seal vulcanizates are shown in Fig. 6. It is observed that the addition of organomodified bentonite slightly decrease the hardness of rubber seal, while the compression set shows irregular pattern. The decreasing of hardness in line with the decreasing different torque and the maximum torque due to plasticizing effect of cationic surfactant.

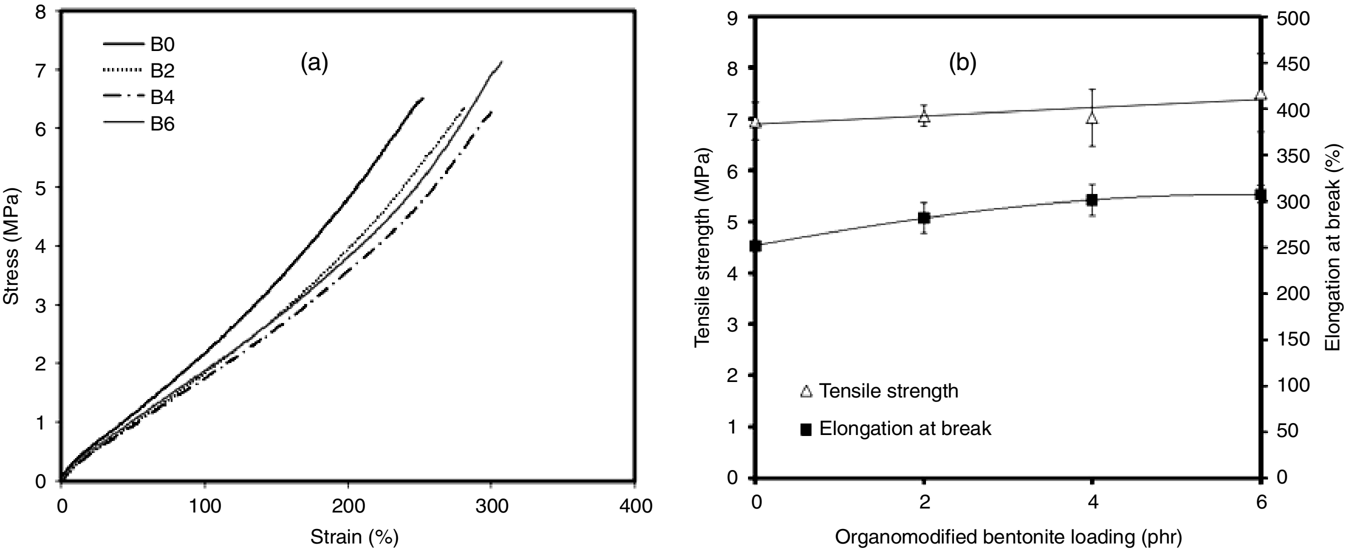

Fig. 5. (a) Tensile curve and (b) tensile properties of NR/NBR rubber seal compound

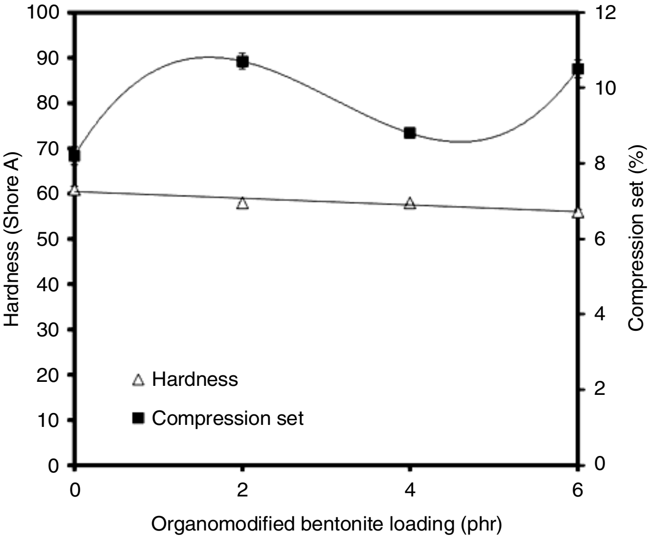

Fig. 6. Curve of compression set *versus* hardness of NR/NBR rubber seal compounds

Sealing performance of rubber seal: The rubber seal LPG system has been built as shown in Fig. 7 based on the actual working condition. The rubber seal is placed in the valve housing of LPG tube with the working pressure 0.7 MPa. The LPG gas will be flowed and contact with the surface of rubber seal (the red colour) then flowed to the rubber hose. The casing is valve housing is imposed as fixed constraints. The boundary condition was determined based on the dimension of rubber seal and the actual working pressure as shown in SNI 7655: 2010.

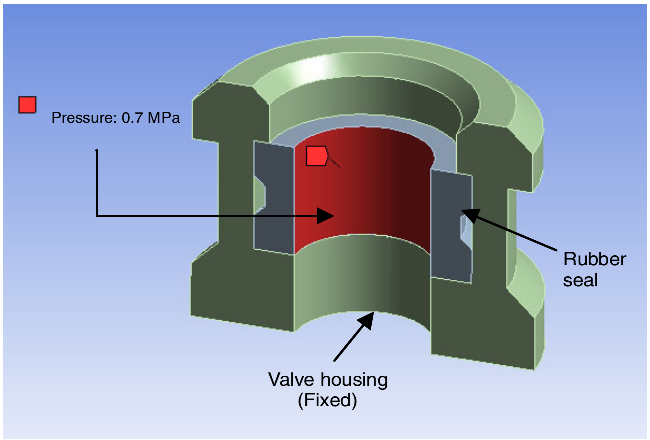

Fig. 7. Boundary condition for the rubber seal LPG

The distribution of contact stress of the rubber seal LPG under actual working pressure of 0.7 MPa are shown in Fig. 8. The contact stress of the middle part of rubber seal LPG is

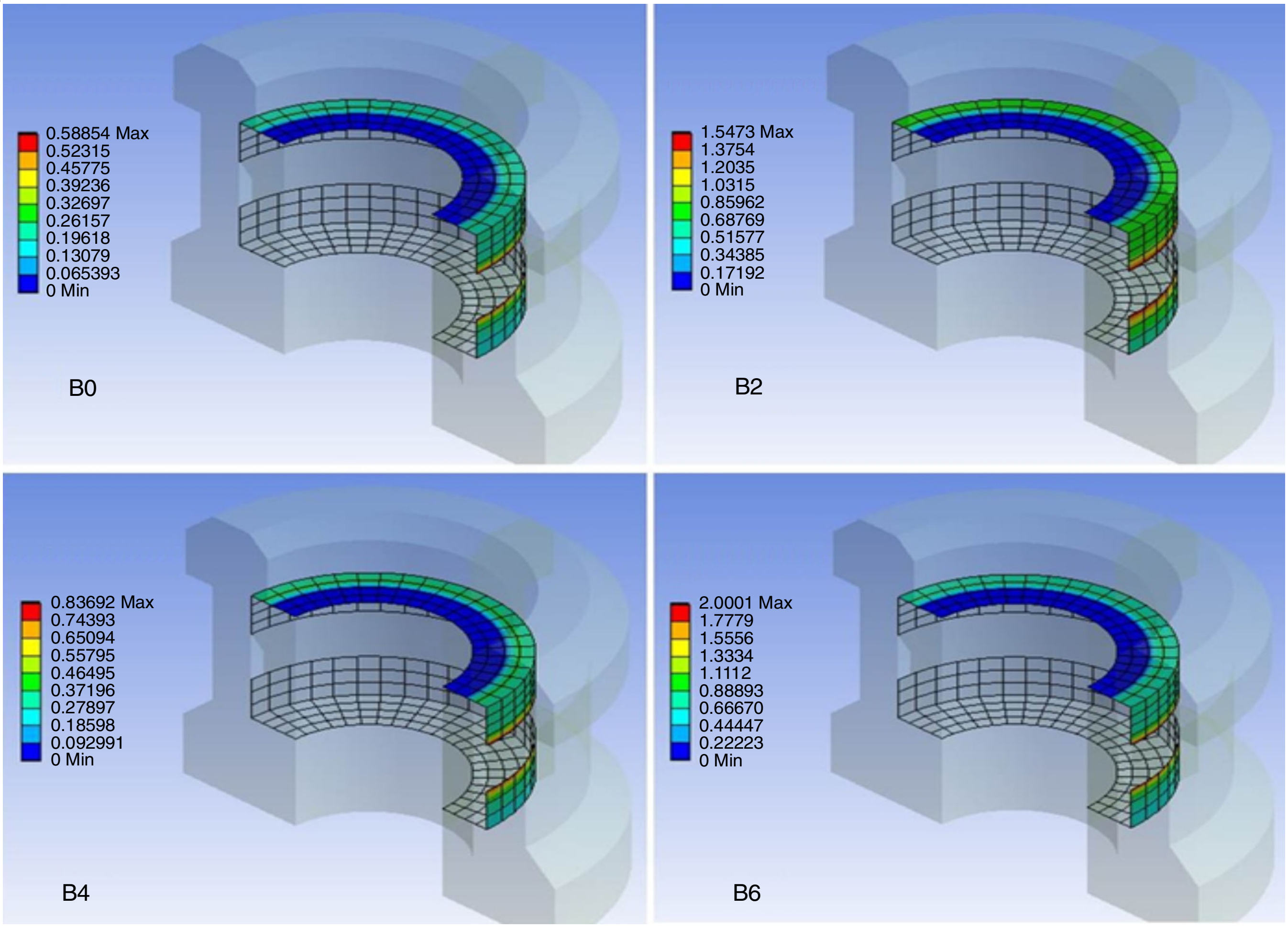

Fig. 8. Distribution of contact stress of NR/NBR rubber seal with and without organomodified bentonite

always higher than the lower and upper part. The maximum value of contact stress is existed in the middle part position of rubber seal. The maximum contact stress of rubber sample B0 (0.588 MPa) is lower than the actual working pressure. Meanwhile for rubber samples containing organomodified bentonite, the maximum contact pressure higher than the actual working pressure. It implies that the good sealing of samples B2 (1.547 MPa), B4 (0.836 MPa) and B6 (2.001 MPa) can be achieved.

The sealing performance of rubber seal LPG is determined using eqn. 2. The effective contact length of all samples similar due the similar dimension of samples rubber seal LPG. The ranking of the sealing performance of rubber seal LPG is : B6 > B2 > B4 > B0.

Misses stress: The misses stress is the important index to evaluate the damage of rubber seal. The higher misses stress value than the actual working pressure, indicating that the rubber seal is a risk of damage. The distribution of misses stress of NR/NBR rubber seal with and without organomodified bentonite is shown in Fig. 9. The distribution of misses stress of all sample are similar. The maximum misses stress is shown on the upper part, outer curve and middle outer of rubber seal LPG, it is due to the flow direction from lower part to upper part of rubber seal LPG. The misses stress value of rubber seal LPG of B2 (0.727 MPa) and B6 (0.792 MPa) is much higher than B0 (0.242 MPa) and B4 (0.347 MPa) under the actual setting pressure 0.7 MPa, which indicates there is a risk of damage. This result is in line with the trend of compression set in Fig. 6. It implies that the compression set is very important parameter for rubber seal LPG.

Conclusion

In this work, the natural rubber (NR)-organomodified bentonite were prepared by the *in situ* organomodified and latex compounding method with varying amounts of bentonite then applied in the silica-NR/NBR rubber seal compounds. By mixing the NR-organomodified bentonite masterbatch into the silica-filled NR/NBR rubber seal compounds, the presence of silica facilitates the exfoliation of organomodified bentonite in the NR/NBR matrix. The NR/NBR-silica/organomodified bentonite show improved silica dispersion physically, as analyzed by Payne effect before and after vulcanization, compared with the NR/NBR-silica reference compound. The presence of organomodified bentonite decreases the vulcanization reaction. The cure rate index, apparent crosslink density and hardness tend to decrease with addition of organomodified bentonite, while tensile strength and elongation at break are enhanced with increasing organomodified bentonite. With an appropriate amount of organomodified bentonite (organomodified bento-

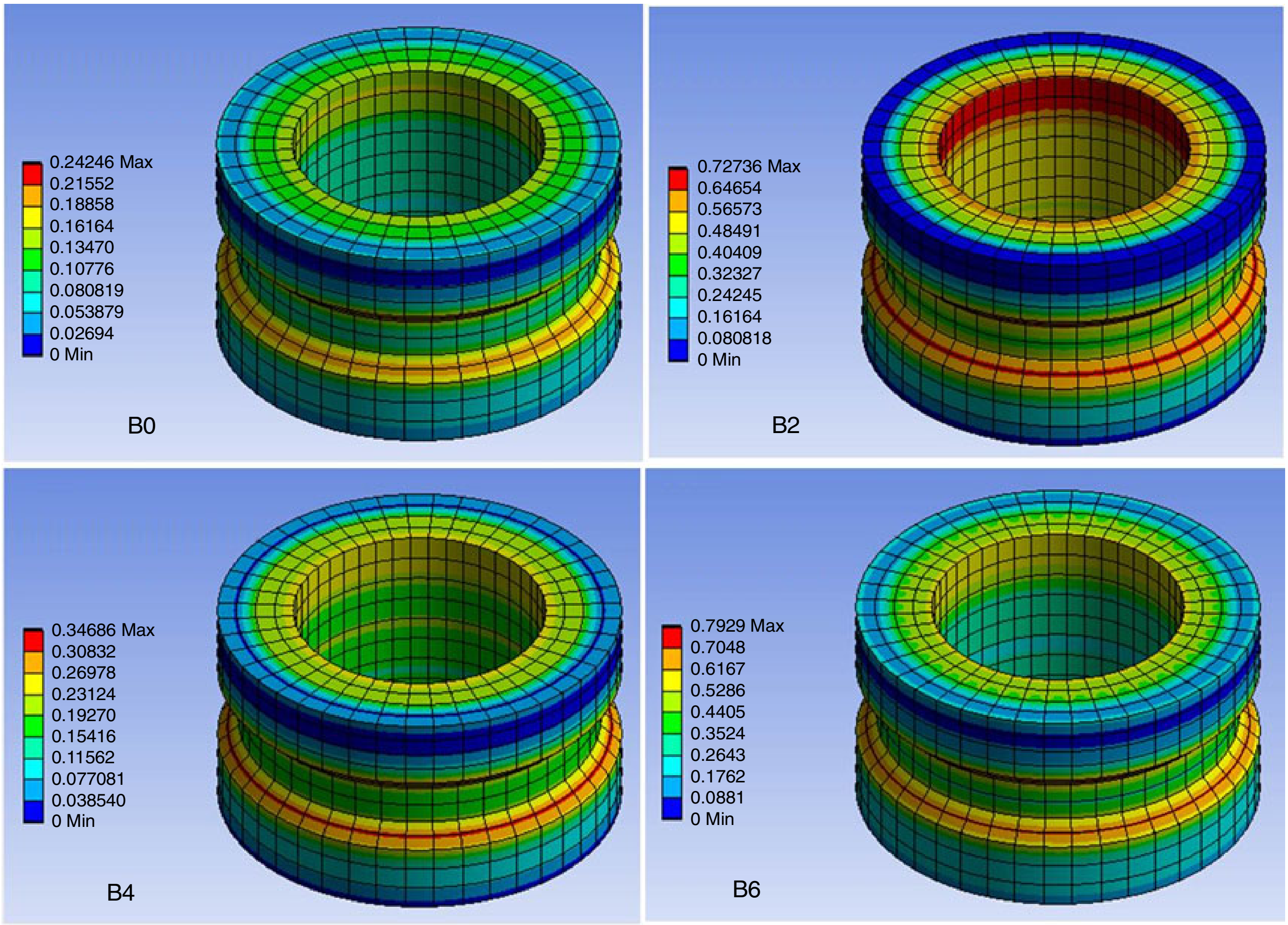

Fig. 9. Distribution of mises of NR/NBR rubber seal with and without organomodified bentonite

nite below 4 phr), the introduction of organomodified bentonite enhances the elastic response of the material, as shown by increasing of tensile properties. From the sealing performance analysis of rubber seal, B4 (4 phr organomodified bentonite) shown best sealing performance and difficult to crack, since the contact stress is larger than the actual working pressure while the misses stress is lower..

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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