Polymer Testing 72 (2018) 377–385

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material Properties

Assessment of failures of nitrile rubber vulcanizates in rapid gas decompression (RGD) testing: Effect of physico-mechanical properties

Mahsa Najipoor[a,b], Leila Haroonabadi[a,b], Ali Dashti[a,b,*]

[a] Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[b] Research Laboratory of Polymer Testing (RPT Lab.), Research Institute of Oil & Gas, Ferdowsi University of Mashhad, Mashhad, Iran

ARTICLE INFO

Keywords:
Nitrile rubber
RGD resistance
Physico-mechanical properties
Crosslink density
Curing system

ABSTRACT

Rapid gas decompression (RGD) test is used to evaluate structural failures such as bubbles, blisters, internal and external cracks in rubber vulcanizates exposed to gas environment under high pressure and high temperature (HPHT) conditions. Physico-mechanical properties of vulcanizates may greatly affect the RGD resistance of rubber products. In this study, effect of the most important physico-mechanical properties such as hardness, modulus, elongation at break, tensile strength, tear strength, compression set and crosslink density of nitrile rubber (NBR) samples cured by different sulfur curing systems including conventional system (CV), semi-efficient system (SEV) and efficient system (EV) on RGD resistance has been investigated. Results showed that the type of sulfur curing system and resultant physico-mechanical properties had pronounced effects on RGD resistance. The NBR rubber samples prepared by CV system exhibited highest failures under RGD testing. Moreover, by increasing crosslink density, hardness and modulus of NBR vulcanizates, the internal cracks were increased during RGD test. Furthermore, the RGD resistance was improved at higher tear strength of rubber samples. Also, lower compression set specially in CV curing system and higher tensile strength of NBR samples lead to less structural failures.

1. Introduction

Nitrile butadiene rubber (NBR) is the copolymer of butadiene and acrylonitrile, and has been widely used in industry over the past years [1–3]. The NBR belongs to the class of specialty elastomers that has notable advantages such as excellent resistance to oils, gases and other fluids over a wide range of temperature, very good resistance to swelling by aliphatic hydrocarbons, low cost, good process ability, wearing resistance, desired processing characteristics and mechanical properties. Furthermore, nowadays the NBR is the standard elastomer mainly used in oil and gas applications such as packer elements, various oilfield seal products, gas barriers, gaskets, sleeves, diaphragms and so on [4–7]. Along with all the benefits mentioned, the presence of unsaturated sites of butadiene units in the NBR makes it susceptible to falling mechanical properties under high operating conditions, hence hydrogenated NBR (HNBR) elastomer could be a good alternative to NBR in order to compensate for this limitation [8,9].

In oil and gas industry, rubber component may be placed under very harsh service environments such as elevated temperature, high pressure and exposure to various gases and fluid for a long time, simultaneously [10,11]. According to these specific operational conditions, the rapid gas decompression (RGD) failure of elastomers can be raised as an important challenge. In this phenomenon that has become known as explosive decompression (ED), explosive decompression failure (XDF), or blister fracture, high pressure gas molecules in contact with rubber component surface, penetrate into it until the elastomer is fully saturated [12–14]. When the gas-saturated rubbers exposed to a rapid gas pressure drop, dissolved gas in rubber network cannot get out quickly and the rubber materials suffer from internal and external fracture such as cracks, bubbles, blisters, and splits caused by the expansion of the absorbed gas and creation of large pressure gradient [15–19]. Actually, due to the high-pressure gas decompression, sub-micrometer-size bubbles were formed in rubber components which by continuing the RGD process, some of these bubbles grew to micrometer-size bubbles and consequently caused crack initiation [20]. In general, the RGD process is relative complex that includes the gas diffusion, dissolution within the elastomeric network, and the extensions of the cavitation in the rubber matrix and eventually crack initiation and crack growth creates various damages in rubber components [21].

Different factors such as test conditions including temperature, pressure, type and composition of gas environment, and decompression rate as well as physico-mechanical properties of elastomer, and the two

* Corresponding author. Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.
E-mail address: dashti@um.ac.ir (A. Dashti).

https://doi.org/10.1016/j.polymertesting.2018.11.002
Received 21 July 2018; Received in revised form 2 November 2018; Accepted 2 November 2018
Available online 03 November 2018

key parameters of gas solubility and diffusivity in elastomer network might control the severity of damages caused by RGD testing [22–26]. Crack damage under RGD test condition is a consequence of a high level of interaction between thermal, diffusion and mechanical phenomena. As mentioned by authors [12,20,25,26] rubber damages under HPHT conditions were influenced by tensile strength which is resistance to crack initiation as well as gas diffusivity and solubility which are driving forces for this phenomenon. These different couplings are difficult to interpret from the experimental results because of the influence of several parameters are not clearly identified [24]. Balasooriyaa et al. [27], stated that the RGD resistance of rubbers depended on main factors including gas permeation and mechanical properties. They studied the effect of solvents, gases and the aging on the RGD resistance of HNBR samples. However, neither details of physico-mechanical properties nor its relationship by RGD testing were reported. Anyway, it seems to be important to address this issue. A study of influencing testing parameters on RGD resistance of HNBR elastomer was investigated by Schrittesser et al. [23], their results showed that increasing the testing temperature, the content of CO_2 gas, and saturation pressure lead to increase of RGD failures under the NORSOK M − 710 standard testing. In general, it is believed that many parameters such as mechanical properties of rubber and gas transport properties including diffusivity nad solubility in rubber network could affect the RGD performance of rubber component [17]. The catastrophic RGD failures occurs at high solubility and low diffusivity. Because of high solubility and low diffusivity causes more gas molecules to be stored in elastomer and the trapped gas would not able to escape from rubber instantly upon decompression step, simultaneously [17,22]. Chen et al. [28] demonstrated that carbon nanotube (CNT) had a direct impact on CO_2 diffusion, solubility, mechanical properties, and further on RGD resistance of HNBR and fluoroelastomer (FKM). So that the use of CNT because of their extremely high modulus, large length/diameter ratio, and small diameter could significantly improve the mechanical properties and reduction in both CO_2 diffusivity and solubility of elastomers. As the lower solubility led to reduction of CO_2 content during decompression step, elastomer containing CNT passed the RGD resistance test with the best ranking as zero rating rank based on NORSOK M-710. Alcock et al. [18] observed clear relationships between the crosslink density, shore hardness, tensile stiffness, and CO_2 permeability of HNBR samples. Based on these results, the gas diffusivity and solubility of HNBR samples were decreased by increasing apparent crosslink density which leads to greater risk of RGD damage on rubber samples. However, it should be noted that the relationship among crosslink density and RGD resistance of HNBR specimens was not presented empirically.

Several studies reported the RGD fracture of elastomeric materials by high pressure gases such as carbon dioxide, argon, nitrogen and hydrogen [14,15,29–32]. High pressure hydrogen decompression failure of O-ring of different rubber materials such as EPDM, NBR, HNBR, and VMQ was evaluated by Koga et al. [12], Yamabe and Nishimura [20,34], Nishimura [26], and Yamabe et al. [32,33]. Based on these XDF studies and investigations, they examined different factors to analysis fracture behaviors of O-ring rubbers. They analyze crack (blister) initiation by changes in chemical structure of rubber composites. Also, they evaluated various parameters for analyzing fracture behavior in rubbers like diffusivity, solubility, critical pressure and tearing energy. Microscopic analysis methods like Optical, SEM, AFM, EDX and etc were part of their studies to investigate rubber fractures. Koga et al. [12] investigated the influences of several factors on crack damage of rubber O-rings under high-pressure hydrogen environment. It was clarified that type of elastomer, temperature, O-ring filling ratio, and decompression time were important factors. By increasing temperature, the tensile strength of rubber O-rings decreased and as a result the resistance to crack initiation was decreased. In addition, Yamabe and Nishimura [34] investigated the relationship among crack damage caused by the mechanical properties of the NBR and EPDM rubbers using various content and type of carbon blacks at a high-pressure hydrogen decompression testing. They found RGD resistance of NBR and EPDM samples depended strongly on tensile properties. They observed crack damages were more severe in both rubber systems with lower elastic modulus and tensile strength.

Since the mechanical properties of rubbers are the criteria for choosing them in different applications under various operating conditions, they can also have a significant impact on RGD resistance of elastomers, so examination of the effects of physical and mechanical properties on rubber performance under RGD testing enables new ways for increasing RGD resistance of rubbers to be revealed. The objective of the present study was to investigate and focus on the relationship among the most important physico-mechanical properties of NBR vulcanizates with their RGD resistance.

2. Experimental

2.1. Materials

The compounding materials used in this study were including 100 phr NBR with 34% acrylonitrile and ML (1 + 4) at 100 °C, 41, purchased from Kumho company, 50 phr high abrasion furnace carbon black: N330 (Pars carbon Ltd., Iran), black granulated powder with nominal particle size of 31 nm and 78 m^2/g surface area. According to our previous studies [35,36] because of excellent physico-mechanical properties of NBR compound samples containing nano particle zinc oxide (ZnO), 3 phr nano ZnO from US Nano material with 99.8% purity and 20 nm average particle size was applied. Sulfur (SU95, Struktol): white yellow powder, density 1900 kg/m^3 was the curing agent and N-Cyclohexyl-2-benzothiazole sulphenamide (CBS) with 95–100 °C melting point and tetramethylthiuram disulfide (TMTD) with melting point 140 °C were curing accelerators. Amount of sulfur, CBS, TMTD and ratio of accelerators to sulfur (A/S) for each sulfur curing system: conventional vulcanization (CV), semi-efficient (SEV) and efficient (EV) are described in Table 1. Other ingredients such as antioxidant: 1 phr N-2-Propyl-N′-phenyl-p-phenylenediamine (IPPD), 5 phr processing oil: dioctyl phthalate (DOP) and 1 phr stearic acid were of commercial grades. Also, toluene for measuring crosslink density was purchased from Iran Shimi company.

2.2. Mixing and vulcanization procedure

Rubber ingredients were accurately weighted and mixed on a laboratory two-roll mill (diameter 25 cm and length 50 cm) at roller temperature of 40–60 °C according to ASTM D3182. The rolls were operated at the friction ratio of 1:1.2. The prepared compounds were allowed to stand overnight at room temperature before vulcanization.

Table 1
NBR compounds formulations with different A/S ratio (phr).

Component/phr	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	N_{10}	N_{11}	N_{12}
Type of sulfur curing system	EV				SEV				CV			
Sulfur	0.5	0.6	0.7	0.8	1	1.2	1.4	1.6	2	2.5	3	3.5
CBS	2	2	2	2	1.5	1.5	1.5	1.5	0.3	0.3	0.3	0.3
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
A/S ratio	5	4.2	3.6	3.12	2	1.67	1.43	1.25	0.4	0.32	0.26	0.23

Then, the rubbers were cured at 160 °C and a pressure of 40 kgf/cm^2 in hydraulic press (SPH-500, Santam, Iran). The vulcanization time corresponds to optimum cure time (t_{90}) obtained from curing curves of MDR rheometer (SMD-200B, Santam Co, Iran). Almost all the curing times were close together, so the total 240 s was selected as curing time for all compounds.

2.3. Sample preparation

For tensile and tear test, for each compounding formulation two sheets with size of 150*150 mm and 2 ± 0.2 mm thickness were cured. Also, cylindrical disk specimens with dimension of height 12.5 ± 0.5 mm and thickness 29 ± 0.5 mm for hardness and compression set tests were prepared. O-rings of 312 standard size with a nominal cross section diameter (CSD) of 5.33 mm were cured for the RGD test.

2.4. Cure characterization and physico-mechanical properties

Cure characteristics and curing behavior were determined by MDR rheometer at 160 °C. The tensile properties such as tensile strength, elongation at break and 100% modulus of NBR vulcanizates for at least 3 dumb-bell shape specimens using die C standard shape were drawn with the following dimensions: (overall length 115 mm, width of grip section 25 mm, reduced section 33 mm and gage length 14 mm) obtained by Santam test machine model STM-20 according to ASTM D412 at room temperature with 500 mm/min crosshead speed. Also, tear test was performed for at least 3 die C specimens in accordance with ASTM D624. Hardness of the specimens was determined according to the ASTM D2240 standard test method using a shore A type durometer. The time used to measure shore A hardness was 3 s. In addition, compression set test carried out for 2 different specimens under 100 °C for 72 h in circulating oven according to the procedure of ASTM D395.

The procedure of ASTM D6814 was followed to measure crosslink density of vulcanizates. At first, density of dry crumb rubber was calculated. Then, the volume fraction of rubber in the swollen gel, V_r, was determined with equilibrium swelling in toluene at room temperature for 3 days. After immersion, specimens dried under 100 °C in a circulating hot-air oven (AP, Froilabo Co., France) overnight. Crosslink density was evaluated by Flory–Rehner equation by implementing equilibrium swelling ratio [37,38].

2.5. Rapid gas decompression (RGD) test

In this work, a high-pressure and high-temperature setup was designed and built to perform a modified RGD test. The image of the experimental testing apparatus of modified RGD is shown in Fig. 1. It consisted of a cylindrical cell (a diameter of 12 cm, and a height of 17 cm), which was made up of stainless steel. The high-pressure cell had a 200 bar maximum working pressure. Also, the working temperature was in the range of 298–573 K. System temperature was controlled by an electric heating element within a jacket surrounding the cell. A PT100 thermometer with a measurement error of ± 1 K and pressure transmitter with a measurement error of ± 0.1 bar were applied to monitor the temperature and pressure variations during a modified RGD test. The high-pressure cell was equipped with safety valve and ball valves. Also high pressure flexible tubes were connected to N_2 and CO_2 gas cylinders to supply a gas mixture containing 10 mol% CO_2 and 90 mol% N_2. In addition, the applied pressure was adjusted by a high-pressure regulator. Also, the experimental data were monitored and recorded by a data acquisition unit.

RGD test procedure was done according to ISO 23936-2 standard [39]. Test conditions were as following: standard 312 O-rings (5.33 mm CSD) were taken under 80 °C temperature, 80 bar pressure, 25–30 bar/min decompression rate and gas mixture containing 10 mol% CO_2 and 90 mol% N_2 for 7 days and 8 cycles.

Fig. 1. Image of apparatus for presented RGD testing.

In order to evaluate damages caused by RGD test in elastomeric parts, each O-ring must be cut to smaller sections (at least four parts) and the cross-sectional area of these smaller sections should be observed in terms of the number of cracks and the total length of cracks. Cross-sectional areas of O-rings magnify by 16-X magnification loupe to investigate existence of any blisters, bubbles and cracks. Then, the rating of RGD test is determined according to procedure of the ISO 23936-2 standard. Samples with no cracks, holes or blisters get a rating of 0 (highest RGD resistance). If total length of cracks is less than CSD length, or any number of internal cracks < 25% CSD, and external cracks < 10% existed, samples get rating 1 and passed the RGD test. Also, by increasing the length of internal and external cracks, rating of RGD increased from 2 to 5. Samples with RGD rating of 4 and 5 fail the RGD test according to mentioned standard procedure.

3. Result and discussion

3.1. Cure properties of NBR compounds

The effect of different A/S ratio and type of sulfur curing system on cure characteristics such as delta torque (ΔM) and optimum cure time (t_{90}) of NBR compounds is shown in Table 2.

As results shown in Table 2, by decreasing the A/S ratio, the ΔM increased due to more formation of crosslink linkage. Therefore, the CV curing system and EV curing system had highest and lowest ΔM, respectively. The values of ΔM could be used as indirect indication of the crosslink density of vulcanizates. It means that sample N_{12} with ΔM = 37.3 value may be presented maximum crosslink density caused by more network formation than other vulcanizate smaples. The corresponding data of crosslink measurement was in agreement with our expectation which is shown in next section by Fig. 2.

3.2. Physico-mechanical properties

Physico-mechanical properties such as crosslink density, hardness, modulus, elongation at break, tensile strength and tear strength affected the quality of elastomeric products. Among these properties crosslink

Table 2
Curing characteristic of NBR samples with CV, SEV, and EV sulfur cure systems.

Component	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	N_{10}	N_{11}	N_{12}
Type of sulfur curing system	EV				SEV				CV			
A/S ratio	5	4.2	3.6	3.12	2	1.67	1.43	1.25	0.4	0.32	0.26	0.23
(dN.m)M_H	10.3	11.7	13.5	15.5	17.2	20.5	21.7	23.1	24.1	27.2	30.7	38.8
(dN.m)M_L	1.2	1.2	1.1	1.2	1.2	1.3	1.3	1.3	1.1	1.3	1.2	1.5
ΔM	9.1	10.5	12.4	14.3	16.0	19.2	20.4	21.8	23.0	25.9	29.5	37.3

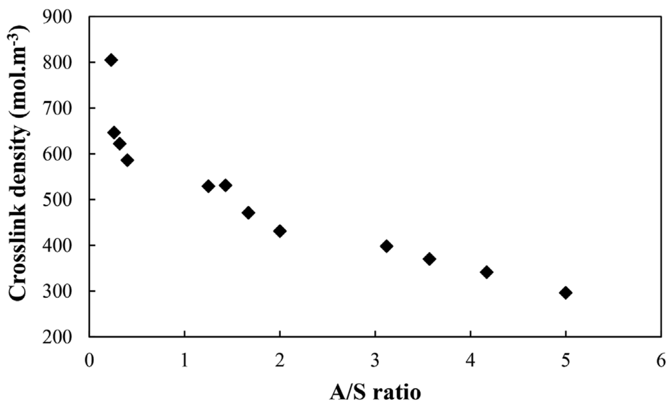


Fig. 2. Effect of A/S ratio on crosslink density of NBR vulcanizates.

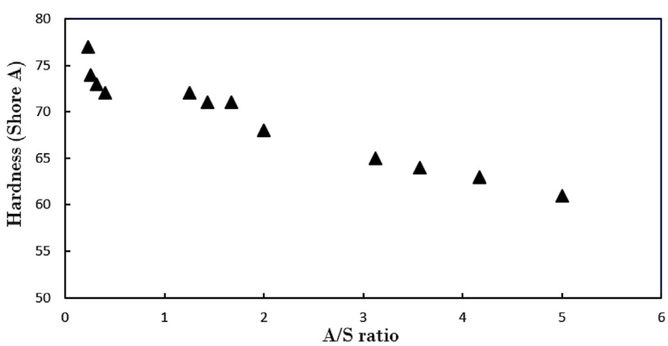


Fig. 3. Effect of A/S ratio on hardness of NBR vulcanizates.

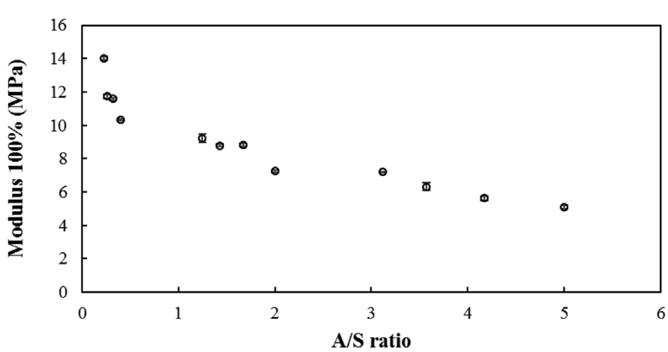


Fig. 4. Effect of A/S ratio on modulus 100% of NBR vulcanizates.

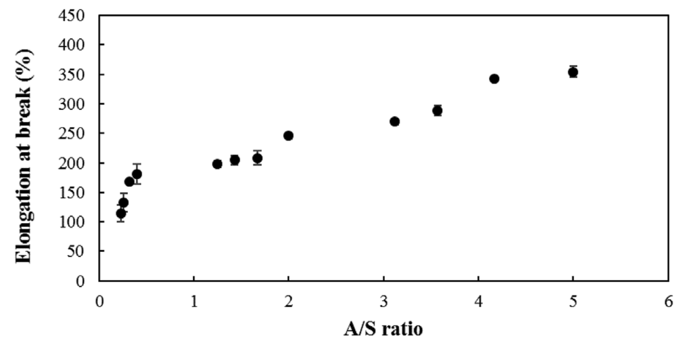


Fig. 5. Effect of A/S ratio on elongation at break of NBR vulcanizates.

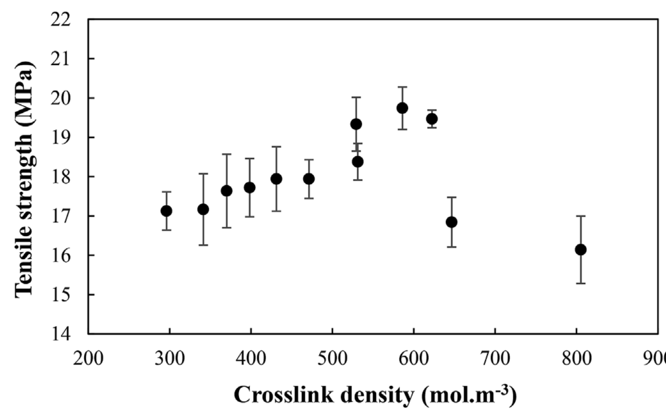


Fig. 6. Effect of crosslink density on tensile strength of NBR vulcanizates.

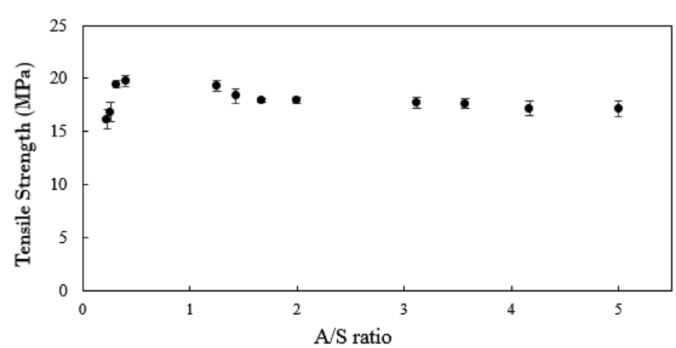


Fig. 7. Effect of A/S ratio on tensile strength of NBR vulcanizates.

density is the most significant factor that effect on other physico-mechanical properties. Crosslink densities of NBR vulcanizates cured by different A/S ratio are shown in Fig. 2. According to Fig. 2, by increasing A/S ratio the crosslink density of vulcanizates decreased. In fact, with decreasing A/S ratio the number of polysulfide crosslinks (C-Sx-C bonds) increased, therefore crosslink density of samples increased. In low A/S ratio, mainly monosulfidic crosslinks (C−S−C bonds) existed that resulted in low crosslink densities. Also, medium values of A/S ratio had disulfide crosslinks (C−S−S−C) and few mono- and polysulfidic linkages [40,41]. Consequently, crosslink density of NBR vulcanized was increased in curing systems in the CV > SEV > EV order.

Fig. 3 is shown the effect of A/S ratio on hardness of NBR vulcanizates. Decreasing A/S ratio lead to increase crosslink linkages and hardness of vulcanizates. In EV curing system by decreasing A/S ratio

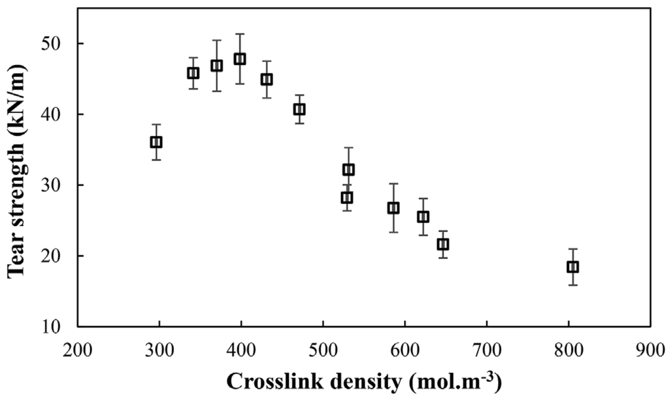


Fig. 8. Effect of crosslink density on tear strength of NBR vulcanizates.

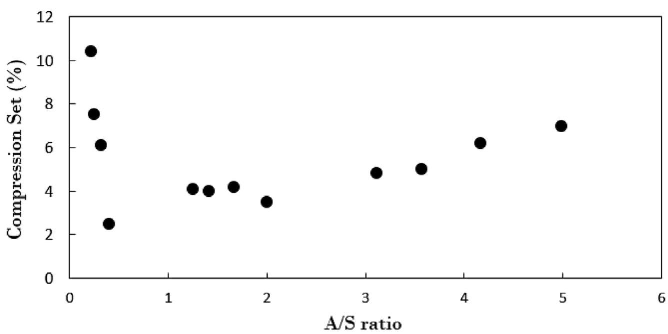


Fig. 9. Effect of A/S on compression set of NBR vulcanizates.

from 5 to 3.1, in SEV curing system from 2 to 1.2 and CV curing system from 0.4 to 0.23 the hardness property changed from 58 to 60, 63 to 68 and 68 to 74, respectively. These data were expected because of more crosslinking of rubber network, resulted in higher hardness of samples.

Fig. 4 is shown the effect of A/S ratio on modulus 100% of NBR vulcanizates. By increasing A/S ratio, crosslink density and the modulus 100% decreased so that maximum value of modulus 100% was around 14.8 MPa for CV curing system and the minimum value about 4.8 MPa for EV curing system.

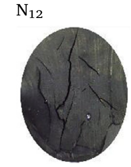
Effect of A/S ratio on elongation at break of NBR vulcanizates is shown Fig. 5. By increasing A/S ratio, elongation at break for vulcanizates frequently decreased. In fact, by increasing crosslink density stretch ability of rubber chains decreased, therefore elongation at break of NBR vulcanizates was reduced. The minimum value of elongation at break was for CV curing system with A/S ratio about 0.23.

Tensile strength is the main characteristic of NBR samples. Many studies have been reported on the effect of crosslinking on the tensile strength of vulcanizates [42,43]. The result of effect of crosslink density on tensile strength of vulcanizates is illustrated in Fig. 6. The tensile strength values passed through a maximum as the crosslink density increased. As demonstrated in Fig. 7, by increasing A/S ratio from 0.23 to 1.2, tensile strength continuously increased and reached to a maximum value in the SEV curing system. As A/S ratio increased from 1.2 to 5, the tensile strength was reduced. This trend can be explained as followed: distribution of the external stresses on rubber network would be improved by increasing crosslinks, as a result, the tensile strength was increased. However, increasing crosslinks over optimum level reduces the average molecular weight between crosslink points and cause localized stresses which results in lower values of tensile strength.

Moreover, tensile strength property is also dependent on crosslinks type. So that polysulfidic crosslinks and monosulfidic crosslinks resulted in higher and lower tensile strength, respectively [1].

The initiation and growth of tear is very important factor in the failure of rubber products. High tensile strength indicates good tear strength. Also, tear strength is an indication for fatigue and abrasion of the rubber, as well as crack growth when the rubber is exposed to sudden stress [44]. Fig. 8 shows effect of crosslink density on tear strength of NBR vulcanizates cured by different A/S ratio. By increasing crosslink density, the tear strength similar to tensile strength passed a maximum value then decreased. In fact, NBR vulcanizates cured by EV curing system that have monosulfide linkages, have high tear strength and crack growth resistance compared to those with di-sulfide and polysulfide linkages (CV and SEV curing system) [45]. Furthermore, according to Figs. 6 and 8 tear strength is more sensitive to increase of crosslink density than tensile strength which these results are in agreement with data obtained by Coran [42] and Kok and Yee [46] for rubber samples.

Table 3
Sections of NBR O-rings after RGD and rating of NBR vulcanizates.

NBR sample	N_1	N_2	N_3	N_4
Section of NBR O-rings after RGD				
RGD Rating	1	1	1	1
NBR sample	N_5	N_6	N_7	N_8
Section of NBR O-rings after RGD				
RGD Rating	1	1	1	1
NBR sample	N_9	N_{10}	N_{11}	N_{12}
Section of NBR O-rings after RGD				
RGD Rating	1	2	3	4

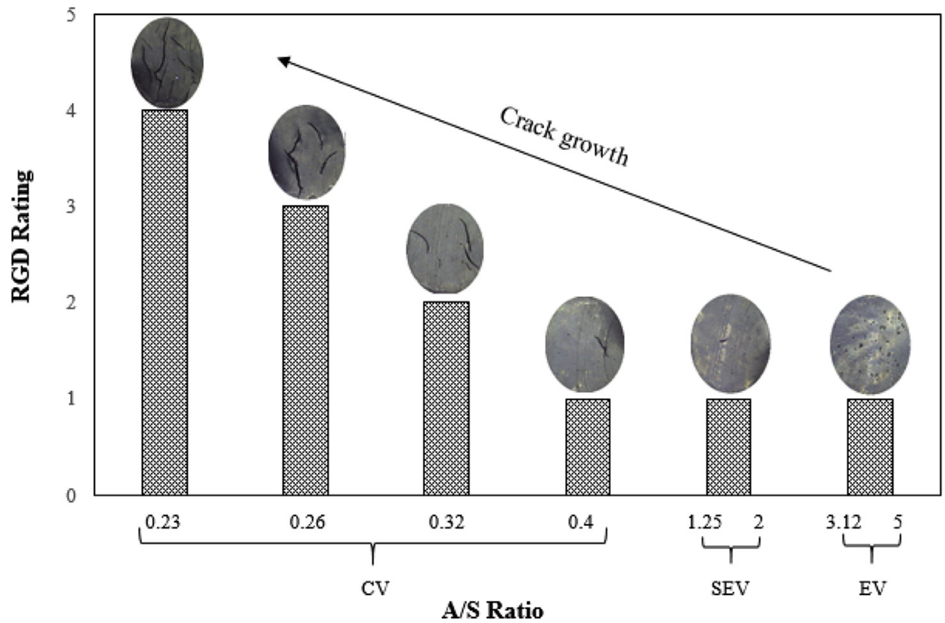


Fig. 10. Relationship between RGD rating and A/S ratio of NBR vulcanizates.

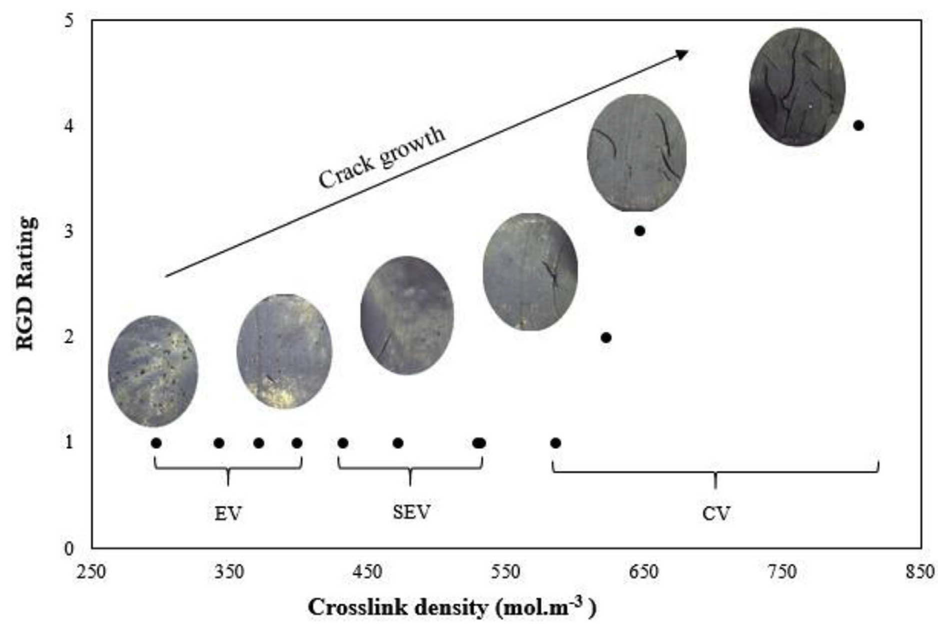


Fig. 11. Relationship between RGD rating and crosslink density of NBR vulcanizates.

Results of compression set (CS) test with the same trend as the work of Jahn and Bertram [47], are shown in Fig. 9. Relationship between the CS and A/S ratio is very important in samples cured by sulfur curing system. In general, the lower temperature conditions of the test and the higher crosslink density, resulted in lower CS [2,47]. Another factor that affects the CS is the type of crosslinking. Monosulfidic linkages show low CS. Therefore, the increase of monosulfidic linkages can improve CS property by decreasing CS values. On the other hand, by decreasing the A/S ratio in CV curing system, the polysulfidic bonds and CS values increase. In the SEV curing system, both mono and disulfide linkages compete, so there was no significant change in the CS values. Although there is a relationship between crosslink density ans CS, it seems to be not only a simple but also a complex relationship. In high A/S ratio, due to insufficient crosslinking linkages, the CS results were relatively undesirable.

3.3. RGD results

For the investigation of the influence of physico-mechanical properties on RGD resistance, high integrity NBR O-rings vulcanizates (practically without any small voids, cracks and blisters) were subjected to the RGD test according to ISO 23936-2 standard procedure. O-rings with the greatest level of damage as a result of RGD test for N_1−N_{12} compounds are shown in Table 3 by comparing the result of RGD resistance of O-rings containing different A/S ratio, it was observed that by the reduction of the A/S ratio the O-rings suffered more damages. It might be deduced that there is a qualitative relation between mechanical properties and crack growth in rubber components. Based on research of Yamabe et al. [20] the crack growth rate would be accelerated if tear and tensile strength were decreased. It is also mentioned by Koga et al. [12] that the degree of internal cracking became more pronounced and the resistance to crack initiation was decreased

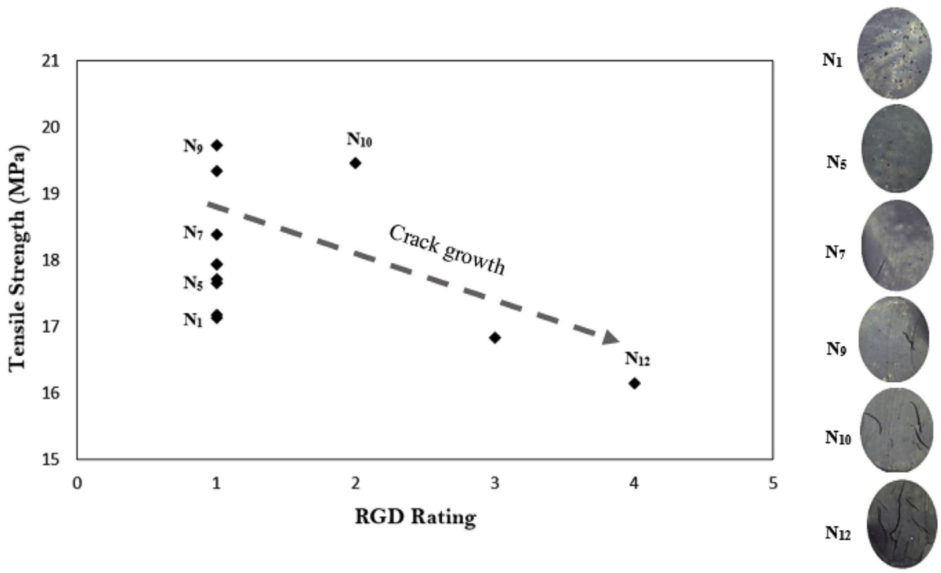


Fig. 12. Relationship between RGD rating and tensile strength of NBR vulcanizates.

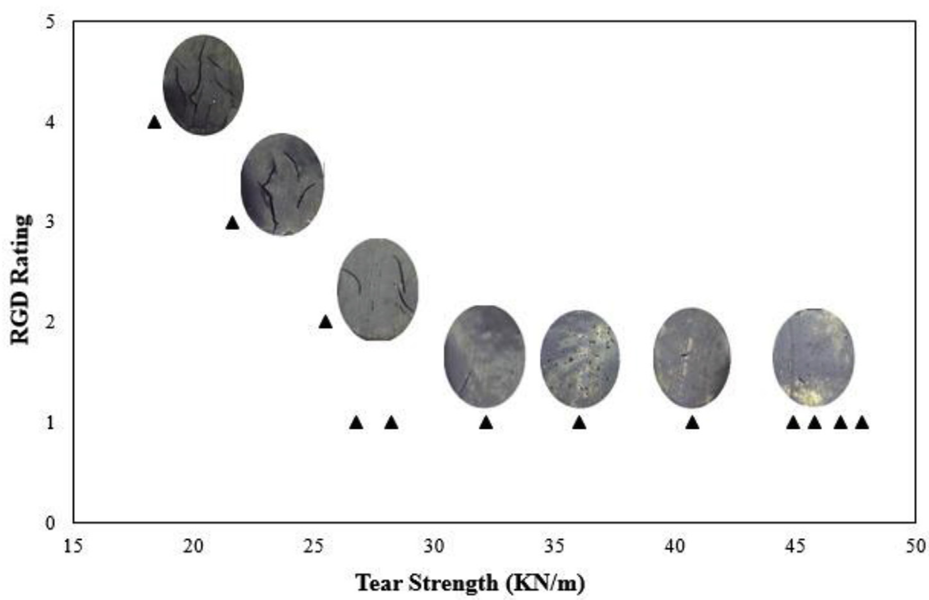


Fig. 13. Relationship between RGD rating and tear strength of NBR vulcanizates.

by decreasing of the tensile strength. The NBR vulcanized by the CV curing system (N_9 –N_{12}) given the high sulfur quantity and, consequently, the high crosslink density, became harder (see section 3.2). Also, tear resistance for N_9—N_{12} vulcanizates is low due to low tear strength values. Since the vulcanized samples with high hardness and low tear strength exhibit less resistance to crack propagation, more cracks were observed in CV curing system, and the number and length of these cracks were increased by decreasing A/S ratio. Thus, the sample N_{12} by rating 4 suffered the most damage and was failed in RGD test. The O-rings cured by SEV curing system (N_5—N_8) due to moderate values of physico-mechanical properties, have the lowest number of cracks and damages during RGD testing and passed the test. According to the obtained results, the most RGD resistance sample with the least damage is N_5 sample with the A/S ratio around 2. This choice is due to its suitable physico-mechanical properties as well as RGD rating. In this system also observed that by decreasing A/S ratio from 2 to 1.2, the crosslink density increased possibly due to the domination of polysulfide linkages to disulfide, hence more crack growth occurred during RGD test as shown in Table 3. In N_1—N_4 O-rings, a large number of cavities were found after RGD test. A reason for the presence of these cavities may be related to low hardness of vulcanizates. By decreasing A/S ratio and increasing hardness of samples, the number of cavities was reduced and only internal cracks were observed instead of those micro-size voids.

A reader may wish to understand direct relationship between fracture behavior, such as RDG rating and physico-mechanical properties according to our presented data in Table 3. Thus, Figs. 10–15 are presented relationship between RGD rating and physico-mechanical properties including hardness, modulus, compression set, tensile and tear strength as well as structural parameters such as crosslink density and A/S ratio of NBR samples. According to these figures, by increasing A/S ratio, crosslink density, hardness and modulus the crack growth of NBR vulcanizates increased. Furthermore, the crack growth was accelerated by decreasing of tear and tensile strength of NBR samples. As shown in Fig 13, the number of internal crack and length of cracks were increased by decreasing of tear strength of rubber samples. Although for

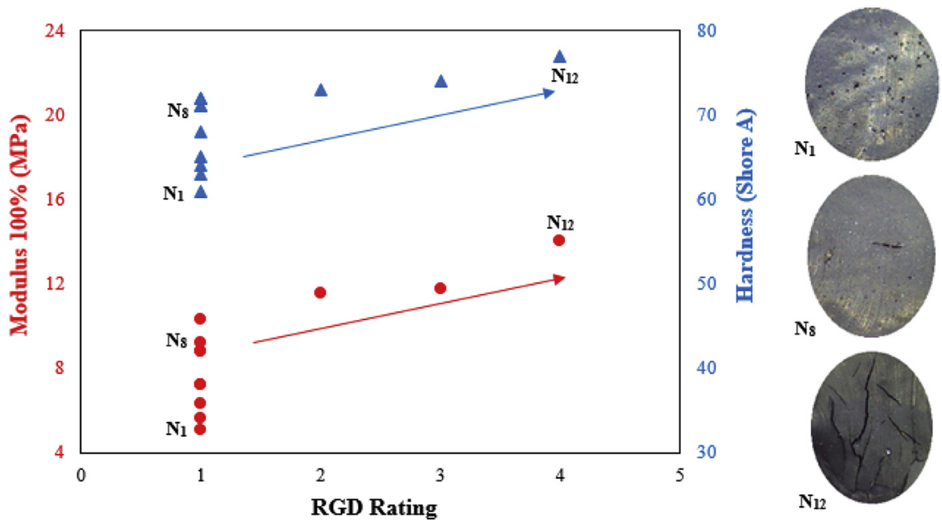


Fig. 14. Relationship between RGD rating and hardness and modulus 100% of NBR vulcanizates.

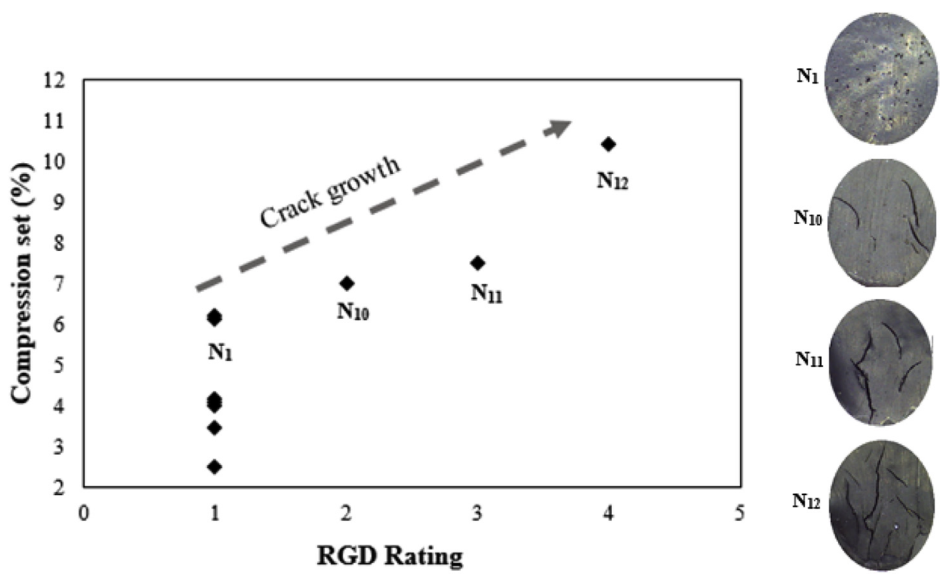


Fig. 15. Relationship between RGD rating and compression set of NBR vulcanizates.

compression set, this relationship is a bit complicated in three curing systems as discussed previously in section 3.2. However, the more crack growth (higher RGD rating) was observed in higher compression set, particularly in the CV curing system as presented in Fig 15.

4. Conclusions

In this study, effect of the most important physico-mechanical properties on RGD resistance of NBR vulcanizates was investigated. It was observed that by increasing crosslink density, hardness, modulus and decreasing elongation at break, the RGD resistance of the NBR vulcanizates decreased. This could be due to penetration of gas molecules through rubber network become more difficult, therefore the number of internal cracks and the length of carcks increased. The lower tear strength caused more damages and cracks during RGD test, therefore RGD resistance of samples improved by increasing tear strength. Furthermore, the NBR vulcanizates with medium tensile strength value had better resistance to RGD. Low compression set particularly in CV system would helped to increase withstand vulcanizates under RGD conditions and result in less damages during RGD test. Presented results show that the NBR samples prepared by the CV curing system and the EV system ones had the worst and the best RGD resistance, respectively. However, in the EV system due to its low crosslink density a lot of cavities were observed that may cause failures during operational conditions. Consequently, the SEV system due to its adequate physico-mechanical properties and good RGD resistance is appropriate choice for NBR products used in engineering applications particularly in oil and gas industries. On the other hand, the balance between most of the mechanical properties and performance testing such as RGD resistance is more satisfied for rubber customers. Therefore, the NBR vulcanizates by SEV system can comprise good RGD resistance as well as very good mechanical properties such as high tensile strength, high tear strength and low compression set at the same time. Finally, it seems to achieve more precise NBR compounding for HPHT applications, the solubility and diffusivity data are necessary. Furthermore, in rubber failure analysis under RGD test the mechanical properties and transport phenomena should be considered, simultaneously.

Acknowledgment

We highly thank the Khorasan-Razavi Gas Company (KhGC) for providing us with polymer testing laboratory (RPT Lab.) facilities to conduct some of tests required in this research study. Also we would specially like to thank Dr. Seyyed Iman Pishbin, head of research & technology at KhGC for his support and assistance.

References

[1] J. Liu, X. Li, P. Zhang, Polym. Test. 54 (2016) 59.
[2] P. Morrell, M. Patel, A. Skinner, Polym. Test. 22 (6) (2003) 651.
[3] S. Chakraborty, S. Bandyopadhyay, R. Ameta, R. Mukhopadhyay, A. Deuri, Polym. Test. 26 (1) (2007) 38.
[4] K.H. Seo, G.M. Kang, D.G. Kim, D.W. Lee, Key Eng. Mater. 703 (2016) 165.
[5] J. Zhao, R. Yang, R. Iervolino, S. Barbera, Rubber Chem. Technol. 86 (2013) 591.
[6] L. Zhao, S. Wang, Y. Chen, W.F. Zhang, Adv. Mater. Res. 418 (2012) 893.
[7] S. Choi, J.C. Kim, J. Ind. Eng. Chem. 18 (3) (2012) 1166.
[8] W.S. Choi, G.W. Kim, J.S. Do, M.H. Yoo, S.H. Ryu, Elastomers. Compos. 46 (2) (2011) 132.
[9] R. Keller, Practical Guide to Hydrogenated Nitrile Butadiene Rubber Technology, Smithers Rapra, UK, 2012.
[10] X. He, X. Shi, M. Hoch, C. Gögelein, Polym. Test. 53 (2016) 257.
[11] R. Mody, D. Gerrard, J. Goodson, Rubber Chem. Technol. 86 (3) (2013) 449.
[12] A. Koga, K. Uchida, J. Yamabe, S. Nishimura, Int. J. Automot. Eng. 2 (4) (2011) 123.
[13] J. Jaravel, S. Castagnet, J.C. Grandidier, G. Benoît, Polym. Test. 30 (2011) 811.
[14] B. Briscoe, T. Savvas, C. Kelly, Rubber Chem. Technol. 67 (1994) 384.
[15] B. Briscoe, S. Zakaria, Polym. Test. 9 (1990) 103.
[16] P. Embury, Sealing Technol 6 (2004) 6.
[17] J.M. Routh, Prediction of Explosive Decompression Damage in Elastomer Seals, Ph.D. Thesis, University of Cranfield, UK, 1999.
[18] B. Alcock, T.A. Peters, R.H. Gaarder, J.K. Orgensen, Polym. Test. 47 (2015) 22.
[19] S.A. Boyer, M.H. Klopffer, J. Martin, J.P.E.J. Grolier, Appl. Polym. Sci. 103 (3) (2007) 1706.
[20] J. Yamabe, S. Nishimura, J. Solid Mech. Mater. Eng. 5 (12) (2011) 690.
[21] Z. Major, R. W. Eng Lang, Failure Anal. 17 (2010) 701.
[22] M.M. Khawaja, Modelling the Permeability of Nitrile Rubber, Ph.D. Thesis, Imperial College, London, UK, 2016.
[23] B. Schrittesser, B. Pinter, G. Schwarz, T.Z. Kadar, T. Nagy, Proc. Struct. Integrity 2 (2016) 1746.
[24] C. Baudet, J.C. Grandidier, L. Cangémi, J. Mech. Phys. Solid. 59 (2011) 1909.
[25] J. Yamabe, S. Nishimura, Int. J. Hydrogen Energy 34 (2009) 1977.
[26] S. Nishimura, Nippon Gomu Kyokaishi 12 (2013) 360.
[27] W. Balasooriyaa, B. Schrittesser, G. Pinter, T. Schwarzc, Polym. Test. 69 (2018) 107.
[28] X. Chen, H.A. Salem, R. Zonoz, Rubber Chem. Technol. 90 (3) (2017) 562.
[29] A. Stevenson, G. Morgan, Rubber Chem. Technol. 68 (2) (1995) 197.
[30] B. Briscoe, D. Liatsis, Rubber Chem. Technol. 65 (2) (1992) 350.
[31] A. Gent, D. Tompkins, J. Appl. Phys. 40 (6) (1969) 2520.
[32] J. Yamabe, T. Matsumoto, S. Nishimura, Polym. Test. 30 (1) (2011) 76.
[33] J. Yamabe, A. Koga, S. Nishimura, Eng. Fail. Anal. 35 (2013) 193.
[34] J. Yamabe, S.J. Nishimura, Appl. Polym. Sci. 122 (5) (2011) 3172.
[35] L. Haroonabadi, M. Najipour, A. Dashti, Proceedings of the 10th International Chemical Engineering Congress and Exhibition, Isfahan, Iran, 2018.
[36] L. Haroonabadi, A. Dashti, M. Najipour, Polym. Test. 67 (2018) 37.
[37] P.J. Flory, Rehner Jr., J. Chem. Phys. 11 (1943) 512.
[38] ASTM Standard D6814–02, Determination of Percent Devulcanization of Crumb Rubber Based on Crosslink Density, Annu. Book ASTM Stand. 09.01, 2013.
[39] ISO 23936-2, Petroleum, petrochemical and natural gas industries, Non-metallic Materials in Contact with Media Related to Oil and Gas Production Part, vol. 2, Elastomers, 2011.
[40] J.M. Vergnaud, I.D. Rosca, Rubber Curing and Properties, CRC Press, Boca Raton, 2016.
[41] T. Lee, S. Morrell, Rubber Chem. Technol. 46 (1973) 483.
[42] A.J. Coran, Appl. Polym. Sci. 87 (2003) 24.
[43] P.J. Flory, N. Rabjohn, M.C. Shaffer, J. Polym. Sci., Part A: Polym. Chem. 4 (4) (1949) 435.
[44] S. Lawandy, S.J. Halim, Appl. Polym. Sci. 96 (6) (2005) 2440.
[45] H. Ismail, R. Jaffri, H. Rozman, J. Elastomers Plastics 35 (2003) 181.
[46] C.M. Kok, V.H. Yee, Eur. Polym. J. 22 (4) (1986) 341.
[47] H. Jahn, H. Bertram, Rubber Chem. Technol. 46 (1) (1973) 305.