JJMIE

Volume 15, Number 4, October. 2021
ISSN 1995-6665
Pages 387 - 393

Jordan Journal of Mechanical and Industrial Engineering

The Effects of Sulfur Content on the Mechanical Properties of Nitrile Butadiene Rubber with Different Aging Conditions

Nabeel Alshabatat[a*], Ahmad Abouel-Kasem[b]

[a]Mechanical Engineering Department, Tafila Technical University, Tafila 66110, Jordan

[b]Mechanical Engineering Department, King Abdulaziz University, Rabigh 21911, Saudi Arabia

Received November 28 2020 Accepted August 15 2021

Abstract

This paper aims to investigate the effects of sulfur addition on enhancing the mechanical properties of Nitrile Butadiene Rubber (NBR) composites. The composites were prepared with the assistance of internal mixer and two-roll mill, and then the speciemns were vulcanized by electrically heated press. The NBR composites were prepared with different sulfur contents (2, 3, 4, 5, and 7 phr). The tensile strength, hardness, compression set, tear strength, and swelling ratio were investigated. The experimental results showed that the addition of sulfur to NBR composites improved their mechanical properties. The unaged NBR composite containing 7 phr of sulfur gives the best 20% modulus (650% improvement), and shore A hardness (27.4% improvement). However, the unaged NBR composites containing 4 phr of sulfur gives the minimum compression set (i.e., 3.2%). Also, adding small amount of sulfur (less than 4 phr) increases the tear strength. The unaged NBR composite containing 2 phr of sulfur gives the best tear strength (106% improvement). The swelling ratio decreases significantly with adding sulfur contents. The unaged NBR composites containing more than or equal to 3 phr of sulfur give 0% swelling. Also, the effects of different aging conditions were investigated. The results showed that NBR composites which were aged in ozone and air degraded more seriously than those aged in oil.

Keywords: Nitrile Butadiene Rubber; sulfur content; rubber aging; mechanical properties;

1. Introduction

Rubbers are extensively used in industrial components (vibration isolators, automotive belts, fuel hoses, oil seals, gaskets, etc.)[1], and can also used in civil engineering applications to improve seismic performance[2]. Fillers and additives are used to control the mechanical properties of rubber, to reduce the cost of rubber products, and to improve rubber processing [1]. Different types of fillers and additives have been considered in rubber production, such as carbon black, silica[2], titanium dioxide [3], carbon fiber [4], carbon nanotubes [5], kaolin [6], nano kaolin [7], hybrid fillers [1], etc. The choice of fillers and additives is closely related to the kind of required properties. In recent years, several researchers have studied the effects of fillers and additives on the mechanical properties of Nitrile Butadiene Rubber (NBR). Carbon black (CB) is commonly used to enhance the mechanical properties of NBR. Mostafa et al. [8, 9] found that increasing CB content, improves the tensile and compressive strength, hardness, compression set ratio, and wear resistance of NBR, on the other hand, increasing CB content can reduce the ductility and swelling ratio. Salkhord and Ghari [10] found that using hybrid filler, which consists of organoclay and nano-calcium carbonate, showed reinforcement of NBR. This filler improved significantly the tensile strength and decreased the swelling coefficient. The effect of using silica and nanoclay as a hybrid filler in NBR was investigated by Salehi et al. [11]. The results showed that this hybrid composite has higher strength and ductility compared to silica or nanoclay filled NBR. Düşünceli et al. [12] investigated the effect of polyurethane (PU) and carnouba wax (CW) on the mechanical properties of NBR coating gloves. They found that adding CW to NBR coating gloves increased slightly the breakage force, and decreased slightly the elongation at breakage, and increased the abrasion resistance. On the other hand, adding PU to NBR decreased the breakage force, and increased elongation at breakage, and decreased the abrasion resistance. Sadeghalvaad et al. [13] studied the effect of adding multiwall carbon nanotubes (MWCNT) and carbon nanofibers (CNF) to reinforce NBR. The results showed that increasing the contents of MWCNT or CNF increased the hardness, and decreased the elongation at break and compression set ratio. However, 5 phr of MWCNT or CNF gave the highest strength of the prepared NBR composites. The effects of waste materials on the mechanical properties of NBR were also studied. Setyarini et al. [14] considered the influence of the addition of waste materials on hardness and tensile strength of NBR. In particular, they investigated the effect of adding rice husk, recycled rubber, and charcoal. They found that the addition of these waste materials led to increase the hardness of NBR. On the other hand, various effects were observed on the tensile strength. For example, rice husk and charcoal led to reduce the tensile strength while the recycled rubber filler

* Corresponding author e-mail: nabeel@ttu.edu.jo.

led to increase the tensile strength slightly. Taib et al. [15] used nanocrystalline cellulose (CNC) as a reinforcement agent in NBR. They found that 5 phr of CNC was very efficient to improve the overall mechanical performance.

Sulfur is a vulcanizing agent which is widely used for chemically crosslinking of unsaturated elastomers. The use of sulfur alone leads to a slow reaction, so the optimal effect of sulfur vulcanization systems is attained in the existence of activators and accelerators [16]. The chemistry of vulcanization is complex and the resulting crosslinks may be monosulfidic (C-S-C), disulfidic ($C-S_2-C$), and polysulfidic ($C-S_x-C$, x = 3-6). The amounts of these bonds depend on the vulcanization system, the cure time, and the temperature. Increasing the ratio between sulfur and accelerators decreases the monosulfidic and increases the polysulfidic [17]. In general, increasing the ratio between sulfur content and accelerator in rubber increases the crosslink density [18]. The structure and density of the crosslinks have a significant influence on rubber composite properties [19]. Several researches have been performed to study the effects of sulfur addition on the mechanical properties of rubber composites. For example, González et al. [17] investigated the effect of using two vulcanization systems (i.e., conventional and efficient) on the physical properties of unfilled natural rubber (NR). High sulfur contents and low accelerator contents are called conventional cure systems, while, low sulfur contents with high accelerator contents are known as efficient cure systems. They found that the tensile and tear strengths are higher for conventional cure systems. Tamási and Kollár [19] investigated the effect of different content of sulfur curing system on the hardness of NR. It was found that the hardness of NR composites increased significantly with increasing sulfur content. El-Nemr [20] investigated the effect of different curing systems on the mechanical properties of NBR composites. The results showed that the crosslink density increased with increasing the contents of sulfur, dicumyl peroxide, dicumyl peroxide/coagent, and radiation/coagent. The NBR composites contained varied contents of sulfur (1, 1.5, and 2 phr) and a fixed content of CB (30 phr). With increasing sulfur content in NBR composites, the hardness, modulus of elasticity, and modulus at a given elongation increased, but swelling ratio decreased.

Most of the rubbers used in industry are frequently subjected to environmental conditions such as elevated temperature, ozone, oil, etc. If the rubbers are subjected to these conditions, their properties will degrade during the time (thermal aging). The main processes during thermal aging are (1) aging due to volatilization and loss of fillers and additives [21], and (2) thermal oxidative aging reactions including crosslink formation, crosslink breakage, main-chain scission, etc. [22]. The crosslinking and chain scission reactions change the network structure. These changes affect significantly the mechanical properties [23]. The effect of aging of NBR on its mechanical properties has been studied for many years. For example, Mostafa et al. [24] studied the effect of CB content on the thermal aging resistance of NBR composites under different aging temperature. They found that thermal aging in oven increased the hardness, decreased the tensile and compressive strengths. However, increasing CB content decreased the aging resistance. Zhao et al. [25] investigated the effect of aging period and temperature on NBR composites using recovery from bending (RFB) test and hardness test. The obtained results showed that increasing the aging temperature and time decreased the RFB% and increased the hardness. The results showed that the aging process passed through three stages; before 60 h, between 60 h and 1700 h, and after 1700 h. In the first stage, NBR lost some additives such as paraffin and antioxidants. In the second stage, further loss in additives occurs and the cross linking plays a dominant role. In the third stage, the cross-linking density is very high and severe oxidation happens and causes chain scissions.

Although extensive researches were carried out to study the effect of fillers and additives on the mechanical properties of Rubbers, the studies on the effects of sulfur addition on mechanical properties of NBR composites are quite limited. To the best of authors' knowledge no article studies the effects of thermal aging resistance of NBR composites with variable sulfur contents. Therefore, the aim of the present study is to investigate the effects of adding sulfur with different amounts (2-7 phr) on the mechanical properties of NBR composites, filled with 50 phr of carbon black, and to determine the effects of thermal aging in oil, in air, and in ozone on the mechanical properties of the prepared composites. The mechanical properties are analyzed in the context of tensile properties, hardness, compression set, tear strength, and swelling ratio.

2. Experimental part

2.1. Materials

The constituent components for preparation of NBR composites include NBR-7150 (28% acrylonitrile, Moony viscosity (ML1+4) of about 51 at 100^{o}C, and specific gravity of 0.98), zinc Oxide (ZnO), stearic acid, carbon black N330, aromatic oil, tetramethyl thiuram disulfide (TMTD), benzothiazole disulfide (MBTS), and sulfur. All the materials used in this study were supplied by the Higher Institute of Rubber, Yanbu, Kingdome of Saudi Arabia. The CB was used as a filler, ZnO and stearic acid were used to activate the curing process, TMTD and MBTS were used to accelerate the cure and control cure rate, sulfur was used as a curing agent, and the aromatic oil was used to help in mixing, calendering, and molding. The specimens investigated in this study were composed of NBR composites with different contents of sulfur according to the recipes shown in Table 1. The code letter S represents sulfur and the subscript represents the amount of sulfur in part per hundred part of NBR (phr).

The mixing of the ingredients was carried out in two steps. In the first step, the NBR, CB, ZnO, stearic acid, and aromatic oil were mixed in the internal mixer. In the second step, the TMTD, MBTS, and sulfur were added to the blend and mixed on a two-roll rubber mill at 75^{o}C. The optimal vulcanization parameters were determined using Moving Die Rheometer (MDR). The vulcanization was carried out using electrically heated press at 140^{o}C for 20 min. Thereafter, the resulted vulcanized NBR sheets were maintained at ambient conditions for 24 hour, then test specimens, were cut from the sheets.

Table1. Formulated composition of NBR composites.

Ingredient	Quantities (phr)					
	S_0	S_2	S_3	S_4	S_5	S_7
NBR-7150 (Low)	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Aromatic oil	10	10	10	10	10	10
Carbon black (330)	50	50	50	50	50	50
MBTS	2	2	2	2	2	2
TMTD	0.15	0.15	0.15	0.15	0.15	0.15
Sulfur	0	2	3	4	5	7

2.2. Aging methods

One objective of this paper is to study the effect of sulfur content on the ability of NBR to withstand the effect of aging under different aging conditions to identify the behavior under degradation environment which rubber usually subjected. Three different aging scenarios were considered (i.e., aging in oil, aging in ozone, and aging in air). Thermal aging of NBR composites was carried out in a temperature-controlled air-circulating oven at 100 ºC for 24 hours. Specimens were either hung in the air (air aging) or immersed in oil tubes open to air (oil aging).Then, the specimens were taken out of the oven, cleaned by tissues, and cooled to room temperature. The aging in ozone was carried out in an ozone climate chamber with an ozone concentration of 200 ppm for 24 hours.

2.3. Testing methods

The tensile characteristics of NBR composites were acquired using a 10 kN capacity tensile tester (AT 10, AlphaTecnologies, OH, USA) based on ASTM D-412 standards [26]. The specimens were cut from NBR composites molded sheets into dumbbell shape using sharp and free of nicks cutting die (gauge length of 33 ± 0.25 mm, width of 6 ± 0.25 mm, and thickness of 2 ± 0.04 mm). The test cross head speed was 500 mm/min. The tensile tests were recorded as the average of three repeated tests for each NBR composite.

The hardness tests were applied according to ASTM D2240 standard [27]. The hardness was measured by using Shore A durometer (RX-DD-4, Electromatic, NY, USA) with an accuracy of 0.1 Shore A. On each specimen, the hardness was measured at five different locations, from which the average Shore A hardness was determined.

Compression set is a measure of the ability of rubber to retain their elastic properties after prolonged compression at constant strain. Compressions set tests were applied based on ASTM D-395 standard [28]. The specimens have cylindrical shape with diameter of 29.0 ± 0.5 mm and thickness of 12.5 ± 0.5 mm. The molding assembly shown in Fig. 1 is used for the tests. It consists of two plates and four bolts to compress the NBR specimens, and two spacers to allow enough clearance for bulging of the NBR specimens. The specimens were compressed to 25% of the initial thickness and the whole assembly was placed in an oven at 100ºC for 24 hour. Then, the specimens were allowed to cool (i.e., allow the specimens to rest on a poor thermally conducting surface such as wood), and then the final thicknesses of the specimens were measured. The compression set percentage was used to measure the permanent deformation and can be given by

$$Comp.set\,\% = \frac{t_o - t_f}{t_o - t_s} \times 100\%\,, \qquad (1)$$

where t_o and t_f are the original and final thicknesses of the specimen, respectively, and t_s is the spacer thickness. The compression set tests were recorded as the average of five repeated tests for each NBR composite.

The specimens of the tear strength were cut into 90 degree angle-shaped specimens and the tests were applied according to ASTM D624 standards [29] using a 10 kN capacity tensile tester (AT 10, Alpha Tecnologies, OH, USA) with cross-head speed of 8.5 mm/s. The testing machine applies a tension force on the specimen until the tear take place some way perpendicular to stress direction. Tear strength is given by $F_{\max}/t$; where $F_{\max}$ is the maximum force required to rip a rubber sample, and t is the average thickness. The tear tests were recorded as the average of three repeated tests for each NBR composite.

Swelling tests were applied based on ASTM D-471 standards [30]. The dimensions of test specimens are 25 mm x 15 mm x 2 mm. Initially, the weights of the dry specimens were measured. Then the specimens were immersed in oil (i.e., Castrol Engine Oil 20w-50) in a heating device at 100º C and for 24 hours. After that, the specimens were removed from the test tubes, the oil was cleaned from specimens' surfaces, and the specimens were immediately weighted. The swelling ratio ($Q\%$) was used to describe the swelling behavior of NBR composites and defined as

$$Q\% = \frac{W_A - W_o}{W_o} \times 100\%\,, \qquad (2)$$

where W_o and W_A are the weights of the specimens before and after swelling, respectively. The oil swelling tests were recorded as the average of five repeated tests for each NBR composite.

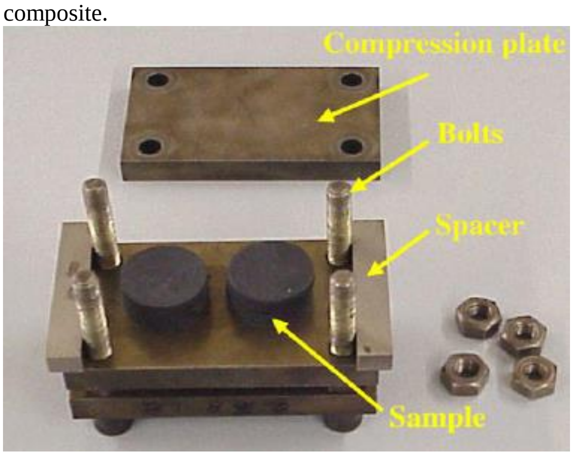

Figure 1. Compression set assembly

3. Results and Discussion

To determine the effect of sulfur addition on the mechanical properties of NBR composites, specimens with different sulfur contents were prepared according to recipes in Table 1. The results of tensile test are represented in Figs.

2 and 3. Figure 2 shows the variation of stress at 20% strain (20% modulus) with sulfur content for different aging scenarios, and Fig. 3 shows the variation of strain at 1.5 MPa-stress. It is clear from Fig. 2 that the NBR composites with sulfur have high strength compared with NBR composites without sulfur. For example, the 20% modulus of the unaged NBR composites with 7 phr sulfur was 4.92 MPa in comparison with 0.65 MPa for unaged NBR composites without sulfur. This might be attributed to the crosslinking density which, in general, increases with increasing sulfur content in rubber [18] (i.e., with increasing sulfur content, the number of sulphidic bonds increases and thus the crosslinking density increases also). The increase of the crosslinking density leads to the reduction of rubber chains mobility. As a consequence, lower strain is observed with adding sulfur (see Fig. 3). For example, the strain, at 1.5 MPa-stress, of unaged NBR composites with 7 phr sulfur was 0.054 in comparison with 1.487 for unaged NBR composites without sulfur.

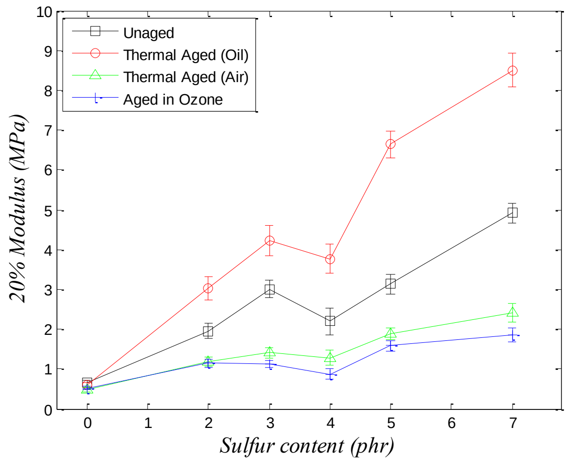

Figure 2. The variation of tensile stresse of NBR composite with different sulfur contentsand aging scenarios at 20% strain (20% modulus).

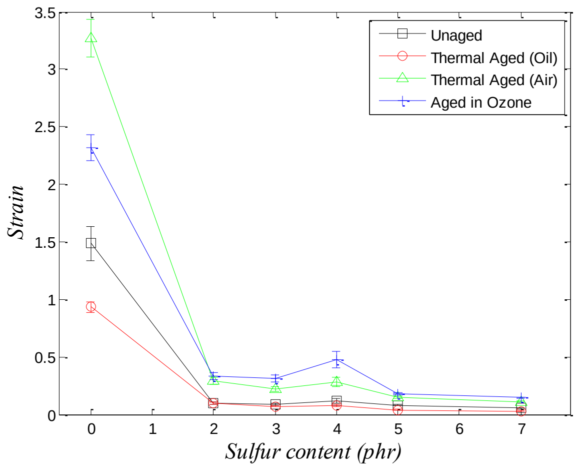

Figure 3. The variation of strain of NBR composites with different sulfur contents and aging scenarios at 1.5 MPa-stress.

During aging, NBR composites lost some additives and fillers [21], and some oxidation reactions occurred such as crosslinking and chain scission [22]. In general, the loss of additives and fillers has a negative effect on the strength of NBR composites. On the other hand, increasing the crosslinks increases the strength to some limit. After that, the higher crosslinking density results in the reduction of the strength (i.e., over crosslinking takes place) [23]. As shown in Fig. 2, thermal aging in air reduced the strength of NBR composites and this might be attributed to the dominant effect of the loss of additives and fillers. However, thermal aging in oil enhanced the strength of NBR composites, and this might be explained as the oil itself adhered to the surface of NBR specimens and formed a protective layer which slowed down the migration and volatilization of the additives and fillers from NBR composites. Also, the oil itself oxidized which lowered the oxygen concentration around the rubber specimens [31]. Thus, the effect of crosslinking is dominant in this case. It is worth to note that, in this study, the accelerating aging processes were carried out for duration of 24 h only. For longer thermal aging period, the crosslinking density becomes very high and severe oxidation happens and causes more chain scissions [25].

The hardness results of the prepared NBR composites are presented in Fig. 4. The results were dependent on the content of sulfur and type of aging. For all NBR composites, the hardness increased by increasing sulfur content, and this results might be attributed to the fact that increasing sulfur content increases the crosslinking density which makes the NBR composites harder. Results with similar trend, for unaged NBR composites, were obtained by El-Nemr [20]. For unaged NBR composites, the highest hardness was 79 ShA for the unaged NBR composites with 7 phr sulfur which is greater than the hardness of the unaged NBR composites without sulfur by 27.4 %.As shown in Fig. 4, aging NBR composites in air and ozone increased the hardness due to the crosslinks formation and the oxidizing layer at the surface of specimens [24]. However, aging in oil decreased the hardness because the oil penetrated into the rubber caused softening for the surface of specimens.

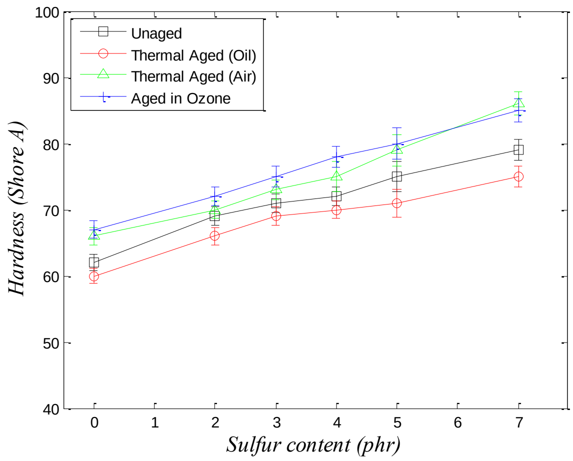

Figure 4. The variation of shore a hardness of NBR composites with different sulfur contents and aging scenarios.

The results of the compression set tests are presented in Fig.5. The figure shows the variations of the compression set percentage of NBR with sulfur contents and type of aging. As shown, the compression set of NBR decreased rapidly by adding sulfur. The results can be interpreted by the increase in the crosslinking density in NBR composites. Therefore, the mobility of the rubber chains decreased. For example, the compression set percentage for unaged NBR composites with 4 phr sulfur content was 3.2% in comparison with 58.3% for unaged NBR composites without sulfur. Aging processes decreases significantly the ability of NBR composites to elastic recoveryafter removing the load. By aging, the crosslinking increased and the network structure became tighter, and thus the compression set increased [32]. The compression set of NBR composites aged in air and ozone is greater than that of NBR composites aged in oil, indicating the more severe degradation. Results with similar trend, for unaged hydrogenated NBR seals, were obtained by Lou at al. [33]. For thermally aged specimens, with increasing sulfur content, the compression set decreased noticeably followed by an increase. The increase of compression set percentage, at high sulfur content, might be attributed to the formation of polysulfidic bonds between rubber molecules. These polysulfidic bonds are more susceptible to cleavage during thermal aging than mono- and disulfidic bonds [17]

The tear strength of NBR rubber composites with different sulfur contents is shown in Fig.6. Tear strength increased with increasing sulfur contents up to 2 phr of sulfure, and then the tear strength decreased with increasing the sulfur contents. For unaged specimens, the maximum tear strength was 35 kN/m, which is 106 % greater than the tear strength of NBR without sulfur. By increasing sulfur content, the crosslinking density increased. Reasonable increasing of crosslinking density improved the tear strength considerably. High crosslinking density (i.e., over-crosslinking) caused unbalanced distribution of crosslinking points and caused stress concentration during loading process, which finally resulted in a reduction of tear strength of rubber composites [17].

In addition to mechanical properties, the capability of NBR composites to swell oil was investigated. Oil swelling has negative effects on rubber. Oil may extract chemicals from rubber or it may chemically react with it which can lead to deterioration of the mechanical properties with time. The results of swelling tests, for unaged specimens, are shown in Fig.7. It can be seen that the swelling ratio of NBR composites decreased significantly with adding sulfur due to the increase of crosslinking density. These crosslinks restrict extensibility of the rubber chains induced by swelling and make it more difficult for oil to diffuse into the gaps between rubber molecules and decrease the swelling percentage. The swelling ratio for NBR composites, with sulfur contents equal or greater than 3 phr, was almost 0%.

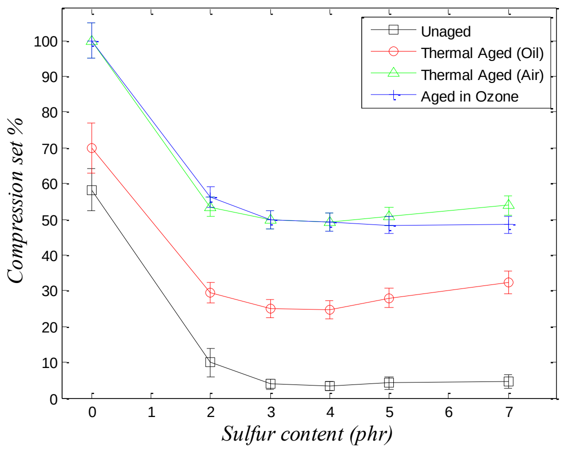

Figure 5. The variation of compression set ratio of NBR composites with different sulfur contents and aging scenarios.

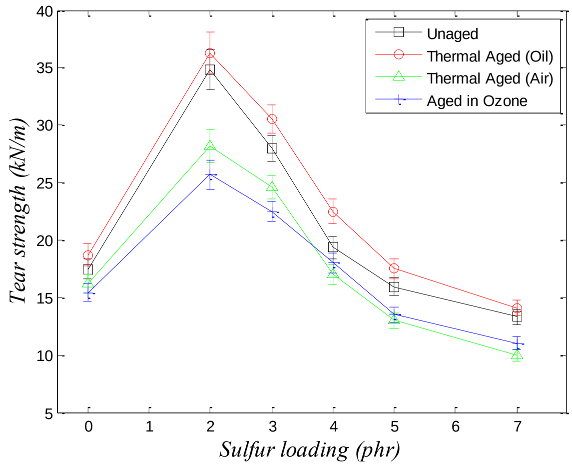

Figure 6. The variation of tear strength of NBR composite with different sulfur contents and aging scenarios.

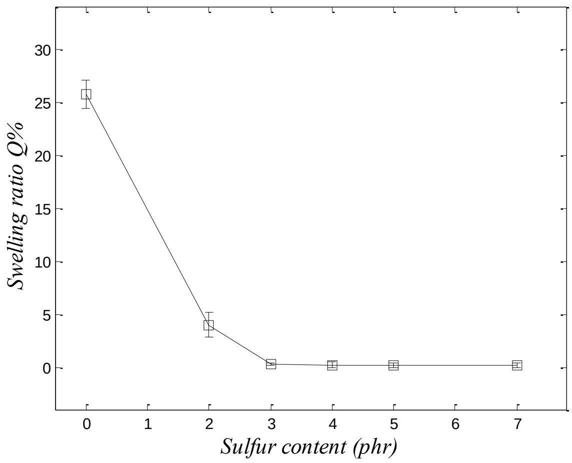

Figure 7. The variation of swelling ratio of NBR composite with different sulfur contents

4. Conclusion

The current work investigates the influence of sulfur contents and aging conditions on the mechanical properties of NBR composites. Tensile, hardness, compression set, tear strength, and swelling properties were examined. Also, accelerating aging of NBR composites in oil, air, and ozone for 24 h was investigated. The following conclusions can be made:

1. Sulfur addition affects significantly the tension properties of NBR composites. In general, the 20% modulus increases and strain at 1.5 MPa-stress decreases with increasing sulfur content. The average 20% modulus of unaged specimens, with 7 phr of sulfur, is 4.92 MPa while that of unaged specimens, without sulfur, is 0.65 MPa. Thermal aging of NBR composites in oil increases the 20% modulus while aging them in air or ozone decreases the 20% modulus.
2. Sulfur addition increases the shore A hardness of NBR composites. The average shore A hardness of unaged specimens, with 7 phr of sulfur, is greater than that of unaged specimens, without sulfur, by 27.4%. The aging of NBR composites in air or ozone increases shore A hardness. On the other hand, the aging of NBR composites in oil decreases shore A hardness.

3. Increasing sulfur content in NBR composites decreases compression set considerably. For unaged NBR composites, using 4 phr of sulfur, decreases the compression set percentage to 3.2%, while the compression set percentage for specimens without sulfur is 58.3%. Thus, NBR composites with sulfur content are very good candidate to use in gaskets, seals, and vibration isolation blocks. Aging of NBR composites in air or ozone increases the compression set and reaches a value of 100% for specimens without sulfur.
4. Tear strength of NBR composites increases by increasing sulfur content and reaches a maximum value at 2 phr of sulfur content. Then, increasing sulfur content decreases the tear strength. For unaged specimens, with 2 phr of sulfur content, the maximum tear strength was 35 kN/m, which is 106 % greater than the tear strength of unaged specimens without sulfur.
5. Adding sulfur to NBR composites decreases significantly the swelling ratio. The swelling ratio reaches 0% when the sulfur content greater than or equal to 3 phr.
6. NBR composites which are aged in ozone and air degrade more seriously than those aged in oil.

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