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POLYCHLOROPRENE BASED RUBBER COMPOSITIONS FOR GASKET PRODUCTION

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Abstract: *Comparison of physical and mechanical properties of four different polychloroprene-based vulcanized rubber compounds has been presented in this paper. Vulcanized rubber compounds containing different amounts of N-(1,3-dimethylbutyl)-N'-phenyl-1,4-benzenediamine (6PPD) as antiaging component (1 phr and 4 phr based on 100 weight of elastomer) and two types of plasticizers (phthalate free adipic acid ester mixture and ether tio ether) had been examined. Mechanical properties of elastomer materials are analyzed after vulcanization and after heat aging in a stream of hot air at 100ºC for 70 hours to determine which rubber compounds would be suitable for non-standard gaskets. Rubber compound with the optimal mechanical properties, e.g. tensile strength is 17.9 MPa, and the optimal resistance against oxidizing agents has been selected as promising material for production of non-standard gaskets.*

Keywords: *elastomer materials, polychloroprene (CR), neoprene, vulcanization, physical and mechanical properties*

1. INTRODUCTION

Due to the specific conditions of exploitation and the risk of fire, non-standard sealing elements made of suitable elastomeric material must fulfill the following requirements:

1. resistance to a very corrosive environment due to the presence of a strong powder oxidizer,
2. resistance to the action of oils, resins, crosslinkers, and alcohol,
3. appropriate physical and mechanical properties,
4. antistatic (in an explosive environment),
5. self-extinguishing,
6. durability at working temperatures up to 80ºC
7. resistance to compressed air pressured up to 8.5 bar or vacuum.

In order to fulfill all of the above requirements, an elastomeric material based on polychloroprene rubber was developed.

2. THEORETICAL PART

2.1. Characteristics of polychloroprene based rubber compounds

Polychloroprene (CR), developed and sold under the trade name Neoprene by DuPont, was the first commercially successful synthetic elastomer. It is produced by free-radical emulsion polymerization of chloroprene (2-chloro-1,3-butadiene). The commercial material is mainly *trans*-1,4-polychloroprene, which is crystallizable [1, 2].

Its structure is shown in figure 1.

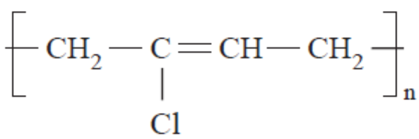

Figure 1. Structure of polychloroprene

Polychloroprenes are noted generally for their good resistance to abrasion, hydrocarbons, sunlight, oxygen, ozone, gas, weathering, and toughness. They have similar mechanical characteristics to natural rubber (NR), including good mechanical strength when it is compounded as a gum vulcanizate. It is more difficult to process than most other synthetic elastomers and has a high resistance to bending.

CR based rubber compound typicaly has tensile strength from 7 MPa to 17.5 MPa, elongation at break from 200% to 600% and hardness from 40 H ShA до 90 H ShA. Like all of the synthetic elastomers, CR is available in a number of grades to aid in compound mixing (blending the raw gum elastomer with a number of other ingredients to make the rubber compound) and to emphasize certain properties.

CR vulcanizates are usually intended for the production of rubber products that are resistant to the action of oxidizing agents (e.g. ozone) and resistant to wear. When aged at high temperatures, vulcanizates become hard and less flexible. With the addition of antioxidants, CR vulcanizates are resistant to aging in a stream of hot air at temperatures up to 90°C.

CR vulcanizates are stable and resistant to swelling in vegetable and animal oils, waxes and lubricants, as well as most aliphatic hydrocarbons, but swell on contact with aromatic hydrocarbons, ketones, esters and chlorinated organic solvents.

At low temperatures, polychloroprene becomes stiff, glass-like and brittle, and it also has tendency to crystallize. The glass transition temperature of CR rubbers and vulcanizates can be lowered using plasticizers, but they may increase the crystallization rate [3].

Since it contains chlorine, rubber products made of CR are self-extinguishing and very resistant to flame. That's why flammable ingredients (e.g. petroleum-based plasticizers) are not used in the production of CR vulcanizates in order to preserve their self-extinguishing.

Polychloroprene elastomers have wide range of applications, ranging from adhesives to wire insulation, depending on its overall durability. The main uses of polychloroprene elastomers are in the fabrication of mechanical rubber goods for automotive products; petroleum production; transportation, construction, and consumer products. The major uses include wire and cable insulation, industrial hoses, conveyor belts, diaphragms, seals, gaskets, O-rings, gasoline tubing, shoe heels, and solid tires. Neoprene latex is used in making gloves, adhesives, and binders.

Based on the above-mentioned properties, polychloroprene is a suitable elastomeric material for the production of non-standard gaskets. CR vulcanizates containing at least 10% carbon black with the addition of antioxidants are used for the production of sealing parts.

2.2 Determination of mechanical and rheological properties of raw gum elastomer and vulcanized rubber

Elasticity and plasticity occur when raw gum elastomer and vulcanized rubber are deformed. Elasticity is the basic property of vulcanized rubber and determines the conditions of exploitation of rubber products. Plasticity defines the technological properties and processability of raw rubber and rubber blends. Determining the mechanical characteristics of rubber is complex, because the character and size of the deformation depend on its amplitude and frequency, load rate and duration, and the ambient temperature. Elasticity includes a number of properties: the ability to retain dimensions and shape, the maximum degree of rubber deformation, the rate of elastic reversible deformation and the ability to reabsorb energy. In practice, it is necessary to evaluate the elastic and deformation properties of rubber. Due to their complex nature, the following elastic and deformation properties may be evaluated:

1. Relative elongation at break,
2. Young’s modulus,
3. Moduli at given elongations,
4. Hysteresis losses,
5. Tear strength.

The level of viscoelastic deformations is determined by elongation or compression at a given load or tear. The rate of deformation is estimated based on the modulus (the stress at a given elongation). The ability to recover elastic deformation is determined by the amount of residual elongation or compression after removal of the load. The ability of rubber to reabsorb energy and the rate of reversible elastic deformation are determined based on the impact elasticity value and are used to characterize the elasticity of the rubber. The strength properties of rubber are most often related to tensile strength and tear resistance. In addition to the tensile strength, the elastic and deformation properties of the rubber are also determined, such as the relative elongation at break and as the moduli at a given elongations.

The hardness of the rubber refers to the resistance to the pressing of metal needles or balls into the rubber, under the action of the compression force of the spring or under the action of weight. To determine the hardness of rubber, Shore's hardness tester, which has a blunt needle connected to a spring, is most often used. The rubber, depending on its composition and degree of crosslinking, has a hardness in the range between 40 H ShA and 90 H ShA. It is known that with an increase in the content of fillers and the duration of vulcanization, hardness increases, while plasticizers decrease it.

Tearing strength (structural strength) is the resistance to the destruction (tearing) of rubber when stretched under conditions of stress concentration. It is determined as the ratio of the force at which the test piece splits and the original thickness of the sample.

Aging is an irreversible change in the properties of rubber under the influence of heat, oxygen, air, ozone, UV light, aggressive substances or constant flexing. After atmospheric aging or heat aging in a stream of hot air, test results are expressed by the aging coefficient, which represents the ratio of changes in tensile strength and relative elongation at the break before and after aging. The smaller change in properties during aging, the smaller aging coefficient. In order to estimate the service life of raw gum elastomer and vulcanized rubber, their properties are examined and compared before and after heat aging. Antioxidants and antiozonants protect rubber against oxidation, while carbon black protects it against UV light.

Based on the results of tests before and after heat aging, a suitable rubber mixture can be selected for the production of non-standard gaskets.

3. EXPERIMENTAL PART

3.1. Gasket properties

Figure 2. is showing the solid rubber polychloroprene ring.

Figure 2. O-ring made of polychloroprene

Based on the available technical documentation, it was determined that it is made of polychloroprene with a hardness of 60±5 H ShA. Due to the aging process, a hardness of 80 H ShA was measured on it. The measured dimensions are Ø 664/661 mm (outer/inner diameter).

3.2. Samples of rubber compounds for non-standard gaskets preparation

Production of raw rubber compounds based on polychloroprene rubber (CR rubber) was carried out at the factory "Tigar Tehnička Guma" a.d. Pirot. Raw rubber compounds marked TG-1, TG-2, TG-3 and TG-4 were produced.

The raw rubber compounds marked TG-1 and TG-2 have the same amounts of *N*-(1,3-dimethylbutyl)-*N'*-phenyl-1,4-benzenediamine as antiaging component (1 phr or part per hundred rubber) and plasticizer (phthalate free adipate esters mixture). The composition of the third raw rubber mixture marked TG-3 has been changed, because it has a higher content (4 phr) of anti-aging agents. The composition of the fourth raw rubber compound marked TG-4 has also 4 phr of anti-aging agents, but different plasticizer (ether tio ether) compared to the other raw rubber compounds. Rubber granulates are preheated on rollers with addition of other ingredients at temperatures between 40°C and 50°C for 30 minutes.

Vulcanization of raw rubber compounds was performed at a temperature of 170ºC for 20 minutes. Vulcanizates in the form of plates and discs are made on a rubber press. Test pieces were cut from the plates and prepared for testing of mechanical properties before and after heat aging. The prepared discs were used as test pieces for testing permanent deformation by compression set at elevated temperature.

Mechanical properties of vulcanizates were tested: hardness, tensile strength, modulus at predetermined elongation, elongation at break and change in permanent deformation by compression set at elevated temperature [4]. For statistical analysis, tests were performed on 7 test pieces for each rubber compound. In addition, density at a temperature of 22ºC and resistance to tearing were determined. The testing of vulcanizates was performed before and after heat aging in a stream of hot air at a temperature of 100ºC for 70 hours, according to the standard requirements. The vulcanizates marked TG-1,TG-2, TG-3 and TG-4 were tested.

Test methods are listed in Table 1.

Table 1. List of test methods

Property	Test method
Density	SRPS ISO 2781:2019, method A [5]
Hardness	SRPS ISO 48-4:2019, type A hardness tester [6]
Tensile strength	SRPS ISO 37: 2019, type 1 dumb-bell test piece [7]
Modulus 200	
Modulus 300	
Elongation at break	
Tear strength	SRPS ISO 34-1: 2017 [8]
Permanent deformation after heat aging (compression set at 100°C for 70 h)	SRPS ISO 815-1: 2021 [9]

4. RESULTS AND DISCUSSION

It is known that vulcanizates based on CR rubbers are very resistant to atmospheric aging, the effect of ozone and other oxidizing agents. When examining the changes in mechanical properties after heat aging of the vulcanizate at a temperature of 100ºC for 70 hours, results are compared with properties for standard quality rubber marked 60 CR.

Physical and mechanical properties of TG-1, TG-2, TG-3 and TG-4 vulcanizates before and after heat aging are presented in Table 2. Non satisfying values are shown in bold.

Table 2. Physical and mechanical properties of vulcanizates before and after heat aging

Physical and mechanical properties before aging	Requirements for 60 CR	Test results			
		TG-1 vulcanizate	TG-2 vulcanizate	TG-3 vulcanizate	TG-4 vulcanizate
Density (g/cm^3)	/	1.39	1.40	1.38	1.39
Hardness (H ShA)	60 ± 5	58	57	58	58
Tensile strength (MPa)	at least 12.0	20.8	18.7	17.9	16.7
Modulus at 200% deformation (MPa)	/	6.4	5.7	6.0	6.0
Modulus at 300% deformation (MPa)	/	12.4	11.3	11.4	11.7
Elongation at break (%)	at least 300	431	421	414	383
Tear strength (daN/cm)	/	45.5	42	48.6	43.3
Changes of mechanical properties after aging at 100ºC for 70 hours					
Hardness (H ShA)	+ 5	**+8**	+6	+4	+ 2
Tensile strength (%)	± 15	-9	-4	0	+ 10
Elongation at break (%)	± 20	**-32**	-5	+6	+ 12.5
Tear strength (%)	/	+10	+1.5	+1.5	+ 10
Permanent deformation (%)	maximum 40	36	37	30	21

TG-1 vulcanizate has satisfying mechanical properties of initial quality according to the 60 CR quality requirements. After heat aging, this vulcanizate has a higher hardness and lower elongation at break than allowed. Therefore, it is suggested to the manufacturer of raw rubber compounds to prepare new samples in order to ensure better mechanical properties after heat aging, in order to achieve the optimal life cycle of the polychloroprene vulcanizate.

TG-2 vulcanizate has satisfying mechanical properties before and after heat aging. It satisfies 60 CR quality requirements. Changes in TG-2 vulcanizate properties show that the hardness is increased by 6 units and the tensile strength is reduced by 4%, which is satisfactory. Vulcanizates based on CR rubber are resistant to bending, so after testing the resistance to tearing before and after heat aging, results are in agreement with literature data for this type of elastomeric material. After heat aging, the resistance to tearing increased slightly (by 1.5%), which confirms high quality.

TG-3 vulcanizate has satisfying mechanical properties of the initial quality and their satisfactory change after heat aging, according to the standard for quality 60 CR. Its physical and mechanical properties are even better compared to the TG-2 vulcanizate. Higher content of the antiaging agent improved the mechanical properties of the tested vulcanizate after heat aging. Hardness is increased by 4 units, tear resistance by 1.5%, and tensile strength remained unchanged. Based on the obtained results, it was determined that the vulcanizate marked TG-3 has good physical and mechanical properties before and after heat aging. The content of added ingredients in this vulcanizate ensures that it has good mechanical properties after heat aging in air at temperatures up to 100ºC.

TG-4 vulcanizate has satisfactory physical and mechanical properties of the initial quality and their satisfactory changes after heat aging, according to the requirements for 60 CR quality. Vulcanized TG-4 compound doesn't have better physical and mechanical properties compared to the vulcanizates TG-2 and TG-3. Higher content of antiaging agent did not significantly improve the mechanical properties of the tested vulcanizate after heat aging. It was found that the hardness increased by 2 units, and the tensile strength and resistance to tearing by 10%. The addition of a new plasticizer has reduced the change in permanent deformation by compression set at an elevated temperature, making this vulcanizate more flexible and tough. The obtained value of permanent deformation is about 21%.

5. CONCLUSION

The initial mechanical characteristics and their changes after heat aging were examined for four vulcanizates marked TG-1, TG-2, TG-3 and TG-4, which are made from raw rubber compounds based on polychloroprene. Based on the obtained test results, vulcanizate TG-3 has optimal mechanical properties before and after heat aging and fully meets the requirements defined by standard for 60 CR. It is shown that this vulcanizate can be a very good material for the production of solid rubber O-rings.

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