The Influences of Environmental Factors on Abrasive Wear of FKM, NBR and CR

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ABSTRACT

Wear resistance is an important factor which influences the working life of many rubber products such as seals and conveyor belts. Most rubber products operate in presence of corrosion, ozone, thermal cycling and heat during the service life. In this experimental study, the influences of environmental factors such as ozone, corrosion, thermal cycling and environmental stress on abrasive wear behaviors of FKM, NBR and CR rubbers were investigated. Abrasion tests were performed to determine tribological properties of samples. The roughness of wear surfaces and hardness of samples were measured. The surfaces of samples before and after exposing ozone were carried out with microscope. The all of the environmental factors caused to decrease of hardness of samples. The volume loss and wear rate values of all samples exposed to ozone increased. The all samples exposed to NaCl solution have highly wear resistance. After ozone tests, the cracks and ruptures from surfaces were occurred in some samples. FKM has the most stress-cracking resistance in the tested materials.

Keywords: Abrasive wear, rubber, ozone, corrosion

Dış Etkenlerin FKM, NBR ve CR Kauçuklarının Abraziv Aşınması Üzerindeki Etkileri

ÖZ

Aşınma direnci, sızdırmazlık elemanları ve konveyör bantları gibi birçok kauçuk ürünün çalışma ömrünü etkileyen önemli bir faktördür. Birçok kauçuk ürün ömürleri boyunca korozyon, ozon, termal çevrim ve ısı etkisinde kalarak çalışır. Bu deneysel çalışmada ozon, korozyon, termal çevrim ve çevresel gerilme gibi dış etkenlerin, FKM, NBR ve CR kauçuklarının abrasiv aşınma davranışları üzerindeki etkileri araştırılmıştır. Numunelerin tribolojik özelliklerini belirlemek için abrasiv aşınma testleri yapılmıştır. Aşınma yüzeylerinin pürüzlülükleri ve numunelerin sertlikleri ölçülmüştür. Ozona maruz bırakılmadan önce ve sonra numunelerin yüzeyleri mikroskop ile incelenmiştir. Dış etkenlerin tamamı, numunelerin sertliklerinin azalmasına neden olmuştur. Ozona maruz numunelerin tamamının hacim kayıpları ve aşınma oranları artmıştır. Tuzlu su çözeltisine maruz kalan numunelerin tamamı, oldukça yüksek aşınma direncine sahiptir. Ozon testlerinden sonra bazı numunelerin yüzeylerinde çatlaklar ve yüzeyden ayrılmalar oluşmuştur. FKM, testedilen malzemeler içinde en çok çatlak ilerleme direncine sahip malzemedir.

Anahtar Kelimeler: Abraziv aşınma, kauçuk, ozon, korozyon

1. INTRODUCTION (GİRİŞ)

The wear occurs in many industrial applications and causes high costs due to material failures. The abrasive wear is a failure problem and it should be taken into account in design and production of components. When materials such as rubbers in work (conveyor belts, seals and tires) are contacting with solid materials, the abrasion will be occurred. Wear resistance is an important factor which influences the working life of many rubber products such as seals and conveyor belts. The tribology of elastomers is expected to play an important role in decreasing friction for minimizing energy loss and decreasing wear for minimizing material loss [1]. In many applications, the abrasive wear is the major failure cause of rubbers [2]. Friction and wear are critical factors in rubber seals [3]. When the assembly of seal is done under rough conditions, the wear of rubber is unavoidable. Thus the abrasion behavior of rubber has attracted attention [4]. The abrasive wear of a rubber seal material may results from many causes which are particulate suspended in lubricating oil, wear debris from inadequate lubrication, corrosion products, airborne dust and rough surface finish. The one of important characteristics of rubber to be used as a seal material is abrasion resistance. The abrasion of elastomer seals reduces life and sealing ability of seals. The elastomeric seals are crucial components which affect reliability and lifetime of all pneumatic and hydraulic devices which are cylinders, valves, rotary and semi-rotary motors [5].

Some of rubber deteriorations are attributable to environmental conditions. The environmental factors reduce durability and service life of rubber components. Most rubber products operate in presence of corrosion, ozone, thermal cycling and heat during the service life.

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The rubber contact surfaces may generate heat during a wear process under harsh environments [6]. The heat resistance of elastomers has a critical role in sealing applications. All rubbers are subjected to deterioration at high temperatures. The high temperature on rubber surface accelerates ageing of elastomer. The ageing is the process of detoration of elastomer properties such as increase of hardness and material cracking [3]. In petroleum and chemical industry, rubber products must be resistance to corrosion. The sea water causes corrosion of rubber seals in marine applications. The fluid leakages can be occurred in rubber seals because of chemical corrosion. While rubber components used in belt conveyors, hydraulic machines etc. are working at outdoor, it is exposed to ozone. The deterioration with time relates to nature of bonds in rubber molecules. In cracking, the molecular bonds are cut. Ozone and ultraviolet light cause degradation of this type. The crack formation depends on temperature, ozone concentration and relative humidity. Because of climate changes the ozone at high concentration can influence the life of rubber components. Even thought the atmosphere contains 0-7pphm ozone concentrations normally, ozone can severally attack non-resistant rubbers [7]. The ozone has an important effect on the abrasion property of unsaturated rubbers [8].

The different types of rubbers such as Natural Rubber (NR), Nitrile Butadiene Rubber (NBR), Fluoro Rubber (FKM), Chloroprene Rubber (CR), Styrene Butadiene Rubber (SBR), Ethylene Propylene Diene Elastomer (EPDM), Hydrogenated Nitrile Butadiene Rubber **(HNBR)** etc. are used as rubber components materials in industry. Although a number of studies have been investigated the mechanical properties of FKM, NBR and CR rubbers, the influence of environmental factors on abrasive wear have not been examined too much. Some researchers have carried out abrasion tests on cylindrical elastomeric sample using suited tribometers. Morrel et al. [9] investigated thermal aging properties of NBR O-rings. They studied compression set tests for NBR O-rings. Wang et al. [10] investigated NBR/nano-Fe_3O_4 composites. Their results showed that the addition of nano-Fe_3O_4 particles improved friction and wear performance of NBR. Poh et al. [8] investigated the effect of ozone on abrasion resistance of epoxized natural rubber (ENR). They showed that the presence of ozone reduced the abrasion resistance of ENR. Fındık et al. [11] investigated the mechanical and physical properties of several industrial rubbers. They considered different ratios of filler materials. They also investigated wear resistance of rubber samples exposed to ozone. Dong et al. [6] investigated the tribological properties of aged NBR under dry sliding. They showed that the aging had a significant effect on the tribological properties of NBR samples.

In literature, there have been a few of investigations of FKM, NBR and CR rubbers subjected to abrasive wear in different working conditions. The effects of temperature and chemical matters on the performance of rubber parts are available in literature. But, the influences of environmental factors on abrasive wear have not been enough investigated until now. The aim of this study is to investigate the influence of environmental factors such as ozone, corrosion, thermal cycling and environmental stress on abrasive wear behaviors of FKM, NBR and CR rubbers. Abrasion tests were performed to determine tribological properties of samples.

2. EXPERIMANTAL STUDY (DENEYSEL ÇALIŞMA)

2.1. Materials and Samples Preparation (Malzemeler ve Numunelerin Hazırlanması)

In this experimental study, industrial rubbers such as FKM, NBR and CR were investigated.

Fluoro Rubber (FKM) has good properties such as heat, oil, solvent, ozone and corrosion resistance. FKM is used in crankshaft and valve-stem seals and military and aerospace seal applications at elevated temperatures [12]. Nitrile rubber (NBR) has exhibited outstanding chemical resistance (oil and solvent) and wide range of operating temperatures [4]. It is used for seals, hoses, fuel-lines and O-rings in automotive industry [2,9]. NBR is also widely used in automobile, transmissions and shock absorbers. These applications require high wear resistance. Chloroprene Rubber (CR) has several technically properties such as good mechanical properties, excellent resistance to heat, ozone and general weather conditions [13]. CR is widely used in automobile industries [14].

The density of samples were measured according to ISO 1183 (Method A) with AND-200 Microbalance and shown in Table 1. In the procedure of density measuring, the sample was weighed in air then weighed when immersed in distilled water at 22°C using a sinker to hold sample completely immersed as required. And then the density of sample was calculated by Microbalance.

Table 1. The density of samples

Material	Density (g/cm^3)
FKM	2,1
NBR	1,2
CR	1,4
Standard rubber	1,1

In sample preparation, the rubber compounds were worked-out by mixing first with kneader than with twin-roll mill. After uniform mixing, the rubber samples were manufactured by compression molding and vulcanized at 170°C, 15MPa for 10min. FKM, NBR and CR samples were provided by Kastas Sealing Technologies Izmir/Turkey for experimental studies. The wear samples have ϕ16mm diameter and 10mm thickness.

2.2. Exposing of Samples to Different Conditions (Numunelerin Farklı Koşullara Maruz Bırakılması)

The elastomers are sometimes exposed to atmospheric environments during the service life. These environmental effects may be at different temperatures.

a)Ozone

Ozone cracks in rubbers develop on surfaces subjected to tensile strain. The rubber conveyor belts and some seals are subjected to tensile strain every time. The ozone is present in the atmosphere at normally 0-7pphm concentrations [11]. In this experimental study, Argentox/Type 3MR model Ozone Test Cabinet was used. The samples were exposed to 50pphm of ozone at 40°C for 48 h. Ozone aging studies were performed to ISO 1431-1 standard [15].

b) Corrosion

Rubber components may be in contact with corrosive materials in chemical plants and marine applications. In this experimental study, tested samples were exposed to 5%NaCl solution (salt water) at 35°C for 400h.

c) Thermal cycling

Thermal cycling is sometimes a serious problem for elastomers. Rubber conveyor belts and seals may be worked at different temperatures. This thermal cycling repeats along the service life. Thermal cycling can be important for some rubber parts in indoor and outdoor conditions. The heat is the one of the aging factors causing degradation. In this experimental study, tested samples were subjected to 120 thermal cycles. The thermal cycling was performed in two separate tanks which contained boiling water and ice-water. The temperature was 100°C at boiling water tank and 0°C at ice water tank. After waiting for 1min in boiling water, samples were waited 1min in ice- water. This operation was a thermal cycle. Samples were dried in an oven at 25°C after thermal cycle.

2.3. Hardness Test (Sertlik Testi)

The hardness tests of samples were performed according to ISO 868 standard with A type Shore durometer (Zwick/Roell model). Hardness tests were performed at 22°C, 12.5N load. The averages of five readings were regarded.

2.4. Abrasion Test (Absaziv Aşınma Testi)

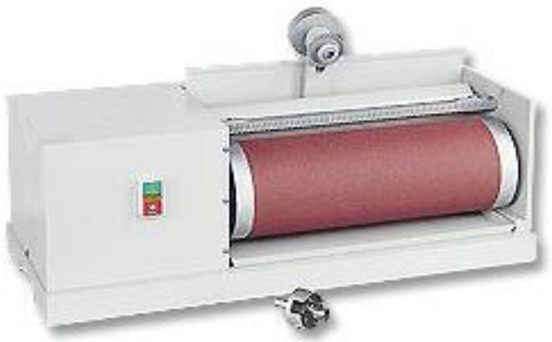


Fig. 1. Wear tester

The abrasion test is a suitable test for measurement of abrasive wear resistance of vulcanized rubbers. Abrasion resistance was evaluated with a standard test according to ASTM D5963 and performed on a DIN Abrader (Ektron Tek Co Ltd, China). In abrasion tester, the test sample is rotated while it is moved laterally across the rotating drum. This working condition assures uniform contact of test sample to abrasive object. The wear tester is shown in Fig.1. In abrasion tester, the sample was pushed against to rotating drum with a specific force (20N) and the rotating drum was covered with an alumina sand paper (#60 grid). The diameter of drum was 150mm and was rotated at 40rpm. The rotation speed of sample was 0,9rpm and abrasion speed was 19,2mm/min. The lateral displacement of sample was 4,2mm per revolution of drum. The sample was moved 40m on rotating drum. 20±2°C temperature and 40±5% humidity were used at test conditions.

Wear is mostly quantified by measuring weight loss of sample [11]. For each test, three samples were used and average value was recorded in order to comply with the standard. The tested samples were weighted using a digital electronic balance before and after abrasion tests to quantify the abrasion wear. The weight loss of tested sample under abrasion test was converted into volume loss using density of sample. In this study, the wear resistance was defined as volume loss in cubic millimeters.

The volume loss was calculated as following according to ASTM D5963:

$$V = \frac{\Delta M . S_o}{\rho . S_w} \tag{1}$$

Here "V" is volume loss of sample (mm^3), "ΔM" is weight loss of sample (mg), "ρ" is density of sample (g/cm^3), "S_0" is nominal abrasiveness of abrasive sheet (200mg) and "S_w" is weight loss of standard rubber (475mg).

The results are also expressed as wear rate. The wear rate values were commonly calculated to use with comparative studies in literature. The specific wear rate was calculated as follows [16]:

$$W = \frac{\Delta M}{\rho . L . F_N} \tag{2}$$

Here "W" is specific wear rate of sample (m^3/N.m), "ΔM" is weight loss of sample (g), "ρ" is density of sample (g/m^3), "L" is sliding distance (40m) and "F_N" is applied normal load (20N).

2.5. Surface Roughness (Yüzey Pürüzlülüğü)

Surface roughness values of wear surfaces of tested samples were performed with Mitutoyo SJ-301 surface roughness tester. Surface roughness of samples exposed to different conditions such as ozone, corrosion and thermal cycling were severally measured.

2.6. **Optical Microscopy** (Optik Mikroskop ile İnceleme)

The surface textures of samples before and after exposing ozone were carried out with a Nikon SMZ 745T Model stereo-zoom microscope (50x).

2.7. Environmental Stress Crack Resistance Test (Çevresel Gerilme Çatlak İlerleme Direnci Testi)

An internal or external crack in a material can be caused by tensile stresses. These cracks can be divided into two groups which are brittle crack and slow crack. The best known type of slow crack is environmental stress cracking (ESC). This type of crack is seen in the presence of surface active wetting agents and stressed samples. The ability of a material to resist environmental stress cracking is known as ESCR. Ray-Ran Model Environmental Stress Cracking Apparatus was used to determine susceptibility of tested samples to environmental stress-cracking when subjected to specified conditions. These conditions contain stress and different environments such as soaps, oils and wetting agents. In this study, first samples were bent and inserted into brackets. Then, samples and brackets were inserted into a tube filled with solution. The tube was placed into heated environment. The cracking failures were inspected periodically. ECSR tests were performed at 50°C.

3. RESULTS AND DISCUSSIONS (BULGULAR VE TARTIŞMA)

Hardness is a good indication of wear property of an elastomeric material. The hardness values of samples exposed to ozone, corrosion and thermal cycling were presented in Fig. 2. In this figure, it was seen that hardness values of treated samples were decreased. The all of the environmental factors caused to decrease of hardness values of rubber samples. The hardness values of NBR samples exposed to thermal cycling were more decreased than other samples. The hardness values of CR samples exposed to corrosion were more decreased than other samples.

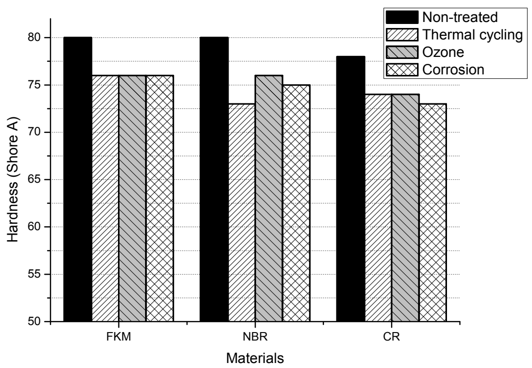


Fig. 2. The hardness values of samples exposed to ozone, corrosion and thermal cycling

The wear of elastomer is a complicated event. It depends on a combination of treatments such as mechanical, mechano-chemical and thermo-chemical. It also depends on configuration of testing device, sliding distance, applied loads and surface property of counterpart. The environmental factors have significant effects on tribological properties and working performance of elastomers. The volume loss values of samples exposed to ozone, corrosion and thermal cycling were presented in Fig. 3. In this figure, it was seen that corrosion reduced volume loss values of all samples. The volume loss values of all samples increased by influences of ozone. The smaller value of volume loss indicates better abrasion resistance. The ozone causes more wear of rubber samples. Wang el al. [10] also stated that the presence of ozone was caused the higher abrasion loss in rubber products.

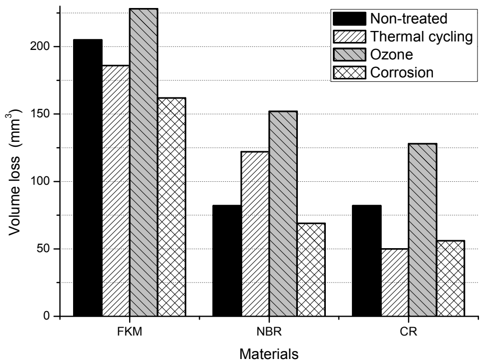


Fig. 3. The volume loss values of samples exposed to ozone, corrosion and thermal cycling

The wear rate values of samples exposed to ozone were presented in Fig. 4. In this figure, it was seen that the wear rate values of all samples were increased by influence of ozone. NBR samples were more worn than other rubber samples. The ozone is one of the aging factors causing degradation. Poh et al. [8] stated that chain scissioning of double bond by ozone generated the greater abrasion loss in rubbers. They also stated that the presence of ozone reduced abrasion resistance of rubber.

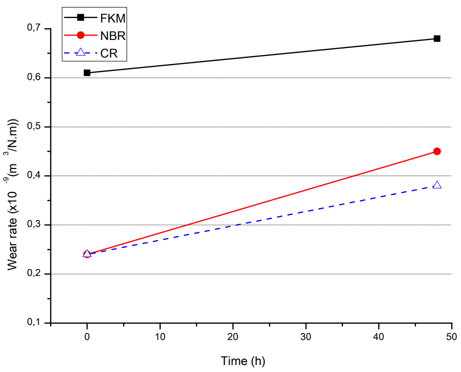


Fig. 4. The wear rate values of samples exposed to ozone

The wear rate values of samples exposed to corrosion were presented in Fig. 5. In this figure, it was seen that the wear rate values of all samples decreased with exposure time. The wear resistance of FKM is better than other samples. The 5%NaCl solution used in experiments didn't have an important corrosive effect on rubber samples. The all samples exposed to NaCl solution have highly wear resistance.

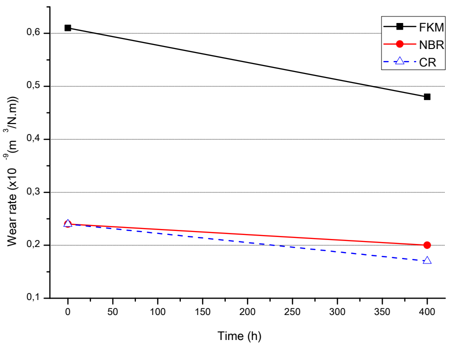


Fig. 5. The wear rate values of samples exposed to corrosion

The wear rate values of samples exposed to thermal cycling were presented in Fig.6. In this figure, it was seen that the wear rate values of FKM and CR samples decreased with exposure time. The thermal cycling decreased the wear resistance of NBR samples and increased the wear resistance of FKM and CR samples. Glaeser and Chandrasekaran [12,13] stated that FKM and CR materials had resistance to heat in their studies. The results obtained from Fig. 6 are similar to their results. The thermal exposure combined with mechanical loading can produce significant damage in polymers [17]. The sample was exposed to thermal stress during the thermal cycles. The thermal cycling induces micro cracks and degradations [17]. A rubber material is generally sensitive to temperature changes. When the temperature increases from 0-100 °C, the anti-fatigue life of rubbers is reduced [6].

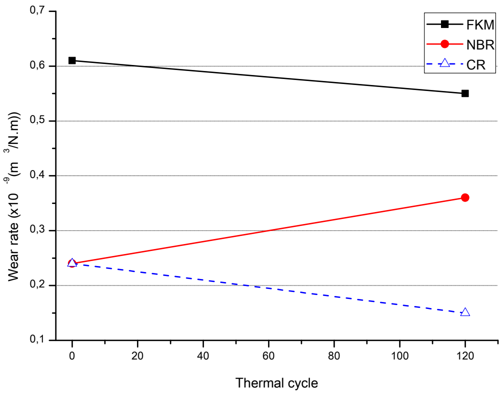


Fig. 6. The wear rate values of samples exposed to thermal cycling

The surfaces roughness values of samples exposed to ozone, corrosion and thermal cycling were presented in Fig.7. In this figure, it was seen that surface roughness values of all samples were increased because of thermal cycling. The all of the environmental factors caused to increase of surface roughness values of NBR samples. When the wear surfaces of rubber samples were examined after wear tests, the significant surface roughness values were observed on surfaces of NBR and CR samples exposed to ozone.

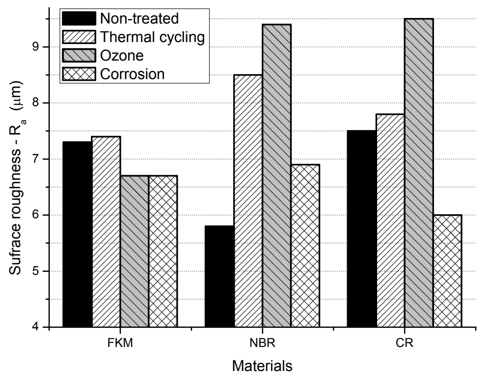
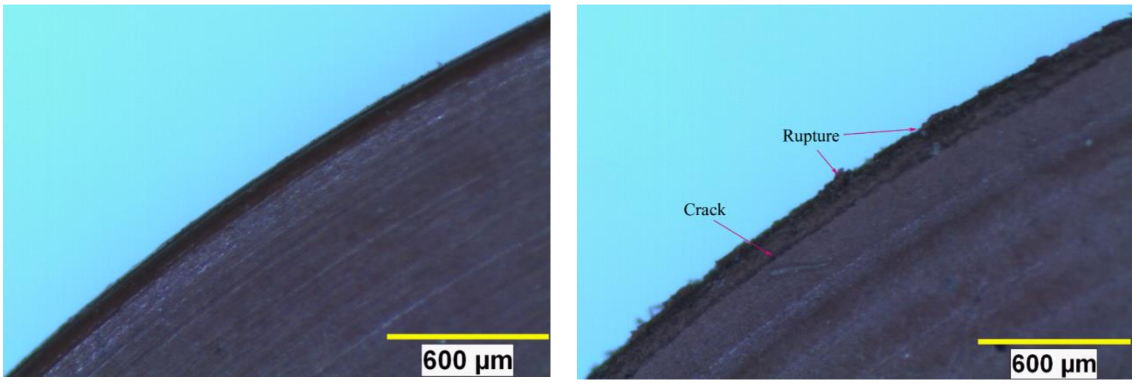


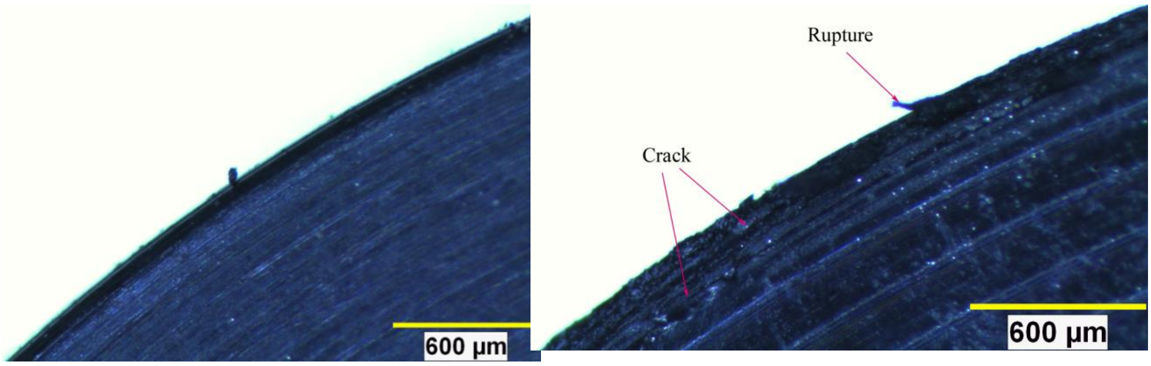
Fig. 7. The surfaces roughness values of samples exposed to ozone, corrosion and thermal cycling

The photographs of samples before and after exposing ozone were taken using a stereo-zoom microscope. Fig. 8-10 show the photographs of ozone cracked surface of FKM, NBR and CR samples. Crack formation can be influenced by presence of oxygen or ozone. After ozone tests, the dense and capillary cracks and ruptures from surfaces were occurred in some rubber samples. When the Fig. 8-10 are analyzed, it is seen that the cracks developed on the surfaces of samples exposed to ozone. Sulekha et al. [7] also stated that a series of cracks were developed in rubbers which were subjected to ozone. When the optical photographs of samples exposed to ozone are investigated it is seen that the cracks are small and discontinuous in CR samples, whereas cracks are deep and continuous in NBR sample.



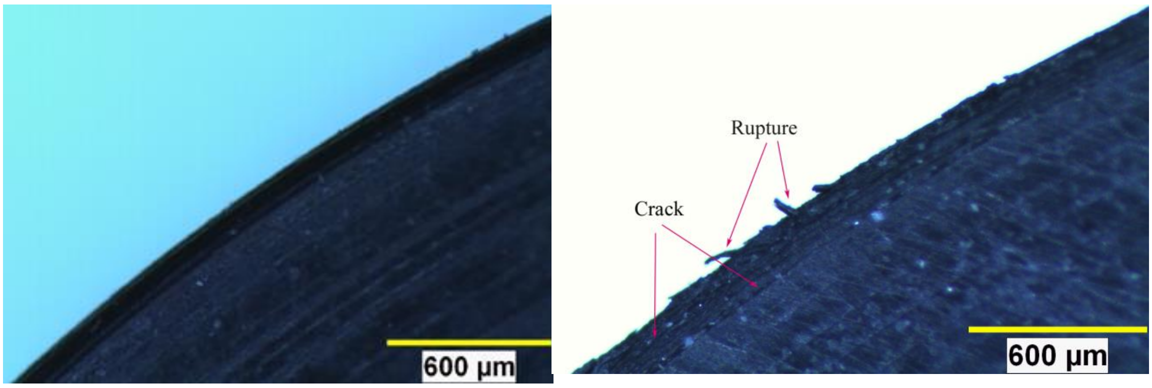
a) non-treated b) exposed to ozone

Fig. 8. The photographs of FKM sample (50x)



a) non-treated b) exposed to ozone

Fig. 9. The photographs of NBR sample (50x)



a) non-treated b) exposed to ozone

Fig. 10. The photographs of CR sample (50x)

Table 2 shows number of failures of rubber samples exposed to environmental stress-cracking test. Fig.11 shows the environmental stress crack resistance of samples. In ECSR tests, crack resistance behaviors of samples were investigated. The stress cracking results in the failure of a material. This situation must be taken into account in design of rubber material parts. FKM has the most stress-cracking resistance in the tested materials. The high stress-cracking resistance of FKM relates to using at elevated temperatures [12].

Table 2. Number of failures of samples exposed to environmental stress-cracking test

	Elapsed time (h)														
Material	0.1	0.25	0.5	1	1,5	2	3	4	6	8	12	16	24	32	48
FKM	0	0	0	0	2	2	5	6	6	7	8	9	*		
NBR	0	1	2	3	6	6	6	6	6	6	8	9	*		

*Stop test since all available samples failed.

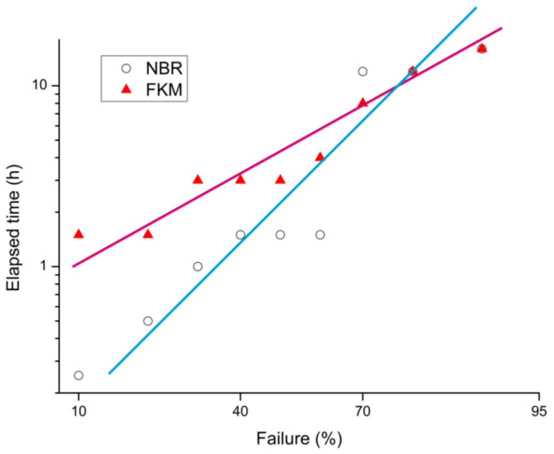


Fig. 11. Environmental stress crack resistance of samples

7- FKM has the most stress-cracking resistance in the tested materials.

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Abbreviations and Symbols		Abbreviations and Symbols	
NR	Natural Rubber	EPDM	Ethylene Propylene Diene Elastomer
FKM	Fluoro Rubber	HNBR	Hydrogenated Nitrile Butadiene Rubber
CR	Chloroprene Rubber	ESCR	Environmental Stress Crack Resistance
NBR	Nitrile Butadiene Rubber	SBR	Styrene Butadiene Rubber
L	Sliding distance, m	ENR	Epoxized Natural Rubber
F_N	Applied normal load, N	S_w	Weight loss of standard rubber, mg
V	Volume loss of sample, mm^3	W	Specific wear rate of sample, m^3/N.m
ρ	Density of sample, g/cm^3	ΔM	Weight loss of sample, mg
		S_0	Nominal abrasiveness of abrasive sheet, mg

4. CONCLUSIONS (SONUÇLAR)

The main conclusions drawn from the present work are summarized as follows;

1- The all of the environmental factors caused to decrease of hardness values of rubber samples.

2- The ozone caused more wear of rubber samples.

3- The all samples exposed to NaCl solution have highly wear resistance.

4- The thermal cycling decreased the wear resistance of NBR samples and increased the wear resistance of FKM and CR samples.

5- The all of the environmental factors caused to increase of surface roughness values of NBR samples.

6- After ozone tests, the dense and capillary cracks and ruptures from surfaces were occurred in some rubber samples.

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