



CHEMICAL COMPATIBILITY OF NITRILE, EPDM AND FLUOR ELASTOMERS FOR OIL AND GAS APPLICATIONS

Caroline Slikta Velloso

Dissertação de Mestrado apresentada ao Programa de Pós-graduação em Engenharia Metalúrgica e de Materiais, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Mestre em Engenharia Metalúrgica e de Materiais.

Orientador: Celio Albano da Costa Neto

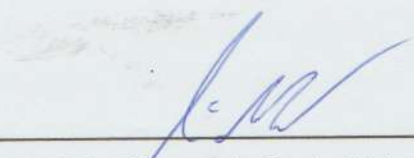
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Examinada por:



Prof. Celio Albano da Costa Neto, Ph.D.



Prof. Renata Antoun Simão, D.Sc.



Dr. Antonio Henrique Monteiro da Fonseca Thomé da Silva, D.Sc.

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COMPATIBILIDADE QUÍMICA DE ELASTÔMEROS NITRÍLICOS, EPDM E FLUORADOS PARA APLICAÇÕES EM ÓLEO E GÁS

Caroline Slikta Velloso

Maio/2019

Orientador: Celio Albano da Costa Neto

Programa: Engenharia Metalúrgica e de Materiais

O presente estudo avaliou a compatibilidade química entre seis elastômeros usados em aplicações de óleo e gás e cinco fluidos. Os testes de imersão tiveram a duração de 8 semanas e a massa, volume e dureza dos elastômeros foram monitorados durante esse período. Xileno se mostrou o fluido mais agressivo de forma geral, levando a variações de massa de até 100% em um caso. O EPDM foi o material mais afetado, as borrachas nitrílicas tiveram comportamento intermediário e as fluoradas, a melhor performance. Ademais, o FFKM não sofreu ataque significativo de nenhum fluido. Para avaliar os efeitos do envelhecimento, testes de relaxação de tensão em compressão foram realizados em borrachas envelhecidas em xileno por 8 semanas. Não houve diferença no perfil das curvas dos elastômeros virgens e envelhecidos, mas o envelhecimento levou ao aumento de rigidez dos materiais. FTIR também foi realizado a fim de identificar as mudanças nas cadeias dos materiais imersos em xileno, porém apenas as borrachas fluoradas apresentaram alguma pequena diferença no espectro.

Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

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OIL AND GAS APPLICATIONS

Caroline Slikta Velloso

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Advisor: Celio Albano da Costa Neto

Department: Metallurgical and Materials Engineering

The present study evaluated the chemical compatibility between six elastomers used in Oil & Gas applications and five fluids. The immersion tests had a duration of 8 weeks and the mass, volume and hardness of the elastomers were monitored along this time. Xylene was the most aggressive fluid overall, leading to mass variation of 100% in one case. EPDM was the most affected material, while the nitrile rubbers presented intermediate behavior and the fluorinated rubbers, the best performance. Moreover, FFKM was not significantly affected by any fluid. For better evaluation of the effects of the ageing, Compression Stress Relaxation tests were performed using the elastomers immersed in Xylene for 8 weeks. No difference on the slope of the curves of the unaged and aged samples was observed, but the ageing lead to increase in stiffness of the materials. FTIR was also performed aiming at identifying the chain modification of the materials immersed in Xylene, and only the fluorinated rubbers presented some small variations on the spectra.

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1 Introduction

Rubbers are widely used in several applications from simple domestic items such as kitchenware to specialized areas as O-rings for Oil & Gas fields [1]. The main use of elastomers is in sealing applications, since this class of material is very resilient, namely, presents the ability of maintaining the elastic behavior by returning to its original shape (and dimensions) after the stress applied is removed [2].

Due to this important role elastomers play, a substantial amount of studies has been performed aiming the better comprehension of its mechanical behavior when submitted to compression stress and, also, when removing this stress.

When submitting the rubber to stress for long periods of time and, specially, in harsh environments and elevated temperature, the material may lose its ability of recovering the original shape. When it occurs, the sealing force is reduced and sealing failure becomes an important issue [2]. For this reason, it is important to study the behavior of the rubber along time, combined with the environment it will be submitted. Generally, Compression Stress Relaxation and ageing tests are performed to assess this behavior.

The acceptable variation of properties is strongly dependent on the application. For sealings, the swelling (gain in volume) may not represent a problem when in contact with liquids. However, the eventual shrinkage when the liquid is removed would lead to leakage and, consequently, jeopardize the functionality. Moreover, the mechanical properties are affected during ageing. As an example, a stiffer material require higher forces to properly seal, so the monitoring of the mechanical properties is important to assure that all the parameters involved in the project are in accordance to the material in all moments during application.

The present study investigated the effects of six different fluids in six types of elastomers. The materials belong to three classes of rubber: nitrile, fluorinated and ethylene-propylene diene rubbers. They were submitted to immersion test for eight weeks, and its mass, volume and hardness variation were tracked along this period. The fluorinated rubbers were the most stable class of rubber, presenting the lowest variations, while the ethylene-propylene diene was the most affected elastomer. Some elastomers immersed in Xylene were submitted to Compression Stress Relaxation tests after total evaporation of the solvent and compared to the performance exhibited by the unaged samples. Overall, no significant different in the Compression Stress Relaxation (CSR) curves were observed. However, 3 out of 4 rubbers showed to be stiffer when aged, presenting a higher F_0 (the maximum stress achieved when performing the CSR tests) when aged than in the unaged condition. To better evaluation and comprehension of the CSR

results, FTIR was performed in the unaged and aged samples. However, only the fluorinated rubbers presented some variation on the spectra of the aged samples.

2 Literature Review

The bibliographic review is divided in two main topics, one concerning the rubbers studied and other concerning the stress relaxation.

2.1 Elastomers

Six elastomers were used in this study and a general information regarding them is presented in this chapter. They are acrylonitrile butadiene (NBR), hydrogenated acrylonitrile-butadiene (HNBR), ethylene-propylene diene monomer (EPDM), tetrafluoroethylene propylene (FEPM or TFE/P), and fluoroelastomers (FKM and FFKM). The different mechanisms of ageing are also addressed in a summarized way for each elastomer. However, it is important to highlight that the chemical compatibility varies according to the application, as well as the tolerances of variations in mechanical properties. The information presented hereby is only general and shall be properly evaluated using the requirements of the final application. For better organization, this chapter is divided by class of elastomers.

The nitrile rubbers (NBR and HNBR) and EPDM are widely studied due to its vast use in several industries and their relatively low cost. FKM presents also a substantial amount of literature due to its better resistance to harsh environments when compared to the nitrile rubber, and presents a lower cost than FFKM and FEPM.

It is important to highlight that there is a great lack of literature when it comes to FFKM and FEPM. It may be due to the extremely high cost of FFKM (at least 50 times higher than FKM), which is a barrier to its study. FEPM, however, is not so expensive as FFKM but still more expensive than the other elastomers, which are already being used in industry. So, the current limited use of those rubbers and the elevated cost may have caused this lack of literature. For FEPM, it was also somewhat difficult to find literature, but the probable reason could not be defined since the cost is similar to FKM. The relative prices of some popular elastomers are presented in Figure 1, while the relative prices of the materials bought for this study are presented in Figure 2. It is possible to observe that, although the relative prices are not exactly the same, they follow the same order from the least to the most expensive.

Relative Prices of Popular Elastomers

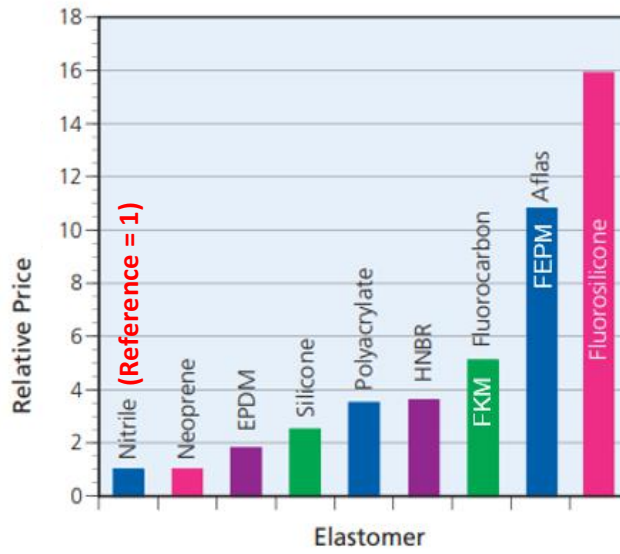


Figure 1 – Comparative prices of elastomers (Nitrile = 1). Adapted from [3].

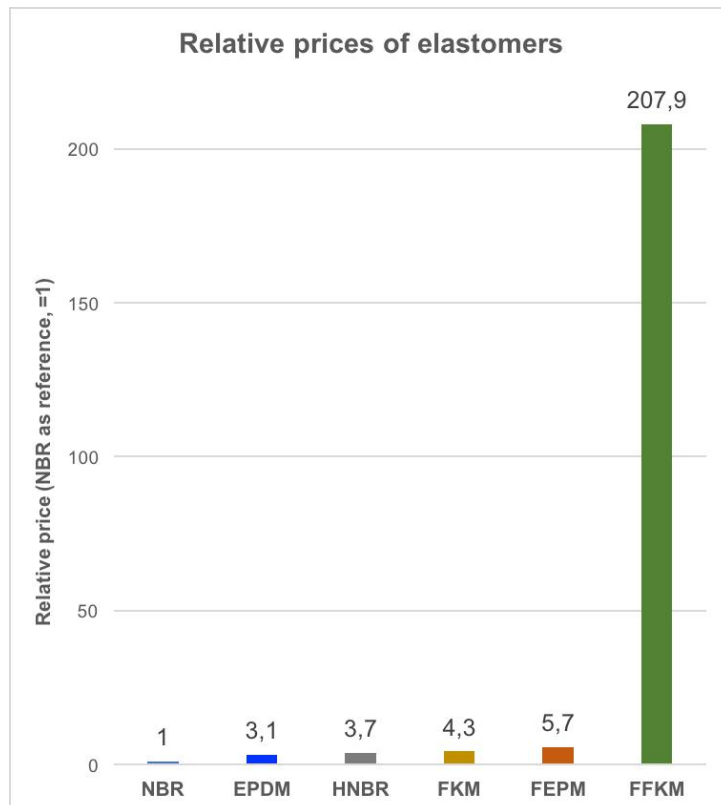


Figure 2 - Relative prices of the elastomers bought for the present study

2.1.1 NBR and HNBR

Both NBR and HNBR are copolymers of acrylonitrile (ACN) and butadiene, and the major difference among them is that HNBR is obtained by catalytic hydrogenation of NBR, so it is called Hydrogenated Acrylonitrile Butadiene Rubber. However, the acronym HSN for Highly Saturated Nitrile is sometimes also used or its commercial name Therban (by Lanxess). NBR is also known as Buna N, Perbunan or nitrile rubber. According to ASTM D1418-17, the letter “R” stands for “rubber”, and the letter preceding it indicates the monomers (N is used for rubbers containing Nitrogen, B for butadiene). The chemical representations of the chains of NBR and HNBR are presented on Figure 3 and Figure 4, respectively.

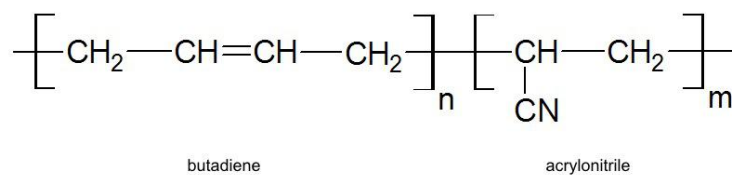


Figure 3 – NBR chain representation (Adapted from <http://polymerdatabase.com/Elastomers/HNBR.html>)

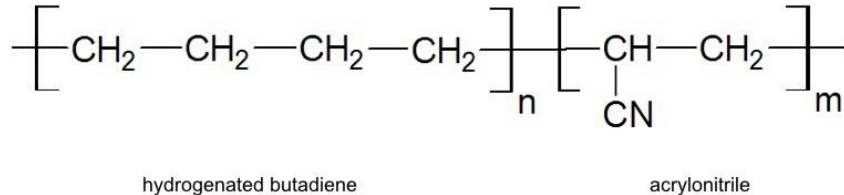


Figure 4 – HNBR chain representation (Adapted from <http://polymerdatabase.com/Elastomers/HNBR.html>)

There are several grades of NBR (more than 150, according to [4]) and the most common grades possess ACN content in the range of 31-35%, but this content can vary from 15 to 51% [5]. This enormous quantity of grades available permits the suppliers to achieve great variety of properties for the final product varying the content of ACN, fillers and plasticizers. Also, it is a point of attention when buying the same elastomer from different suppliers, since the properties will probably not be exactly the same and, then, may lead to some unexpected performance in service.

The most common filler of NBR is carbon black due to the improvement of properties that this component provides, including chemical resistance, tear strength, low compression set and good processing properties. Some non-black fillers may also be used, and the main types are silica, silicate, clay, talc, calcium carbonate, barium

sulphate, titanium dioxide, aluminum trioxide, antimony trioxide, magnesium hydroxide and zinc oxide [6]. Referring to plasticizers, only the polar ones can be used efficiently with nitrile rubbers due to the polarity of this elastomer. As mentioned above, increasing the ACN content lead to higher polarity of NBR, and this phenomenon make the elastomer less compatible to plasticizers in those configurations [7].

The working temperature is in the range of -45°C to 125°C [5], although it will vary according to ACN content (the lower content lead to lower minimum temperatures).

One way to improve tensile strength is by crosslinking, and this class of elastomer is effectively crosslinked by ionizing radiation. Those C-C crosslinks formed provides good elastic properties and are resistant to thermal aging, although do not provide satisfactory dynamical properties [8].

Hydrogenated acrylonitrile butadiene (HNBR) presents excellent mechanical properties, such as tensile strength, tear, modulus, elongation at break and abrasion. Also, this elastomer bears rapid gas decompression in a wide range of temperature. Working temperature range is generally between -40°C and $+160^{\circ}\text{C}$, but these values varies according to the grade chosen [5].

Typical working temperature range of HNBR is -25°C to 160°C , but these values vary according to ACN content and level of hydrogenation. When peroxide or Sulphur cured, it withstands higher temperatures and presents better compression set [7].

HNBR is not sensitive to oxidation and Sulphur attack since it presents a lower level of unsaturation than NBR because of the hydrogenation of butadiene units [9]. Its chemical and mechanical properties are directly related to the content of acrylonitrile and the level of hydrogenation of butadiene units.

Carbon black is also the major filler of HNBR and many plasticizers used for NBR may also be used for HNBR, as long as it withstands higher temperatures and are not so volatile to decrease the heat resistance of the elastomer.

Mechanical properties

The mechanical properties of NBR and HNBR used in this study are presented on Table 1. The information was retrieved from the supplier's datasheet. It is important to note that these values are for information only and must not be used for projects since it is not obligatory the same as the material acquired.

Table 1 - Mechanical properties of NBR and HNBR used in this study.

	<i>NBR</i>	<i>HNBR</i>
Hardness	87 Shore A	88 Shore A
Tensile Strength	3149 psi	3219 psi
Elongation at break	100%	107 %

Chemical compatibility

NBR has polar nitrile groups so the content of acrylonitrile (which varies from 18 to 50%) has great influence on the polarity and, consequently, on the swell of non-polar solvents. Whelan and Lee [7] stands that the good swelling resistance of this elastomer “is restricted to non-polar or slightly polar substances such as mineral oils liquid fuels with low aromatic contents”. Generally, the NBR presents good resistance to oil, but the ageing resistance is limited because of the unsaturated backbone of the butadiene part and, consequently, is influenced by the ACN content [9]. The nitrile rubbers usually present very good resistance to alkaline chemicals, but also usually present satisfactory resistance to acid chemicals [10].

NBR is not resistant to polar fluids, such as esters and ketones. Moreover, the swelling resistance to fluids containing aromatic hydrocarbons is severely diminished if the fluid is modified with alcohols [7].

Regarding swelling, the greater the acrylonitrile content, the lower the phenomenon due to increase in crosslink in polymer backbone [11]. As this content grows, the resistance to oil and fuel is improved and the swelling in motor fuels, oils and fats decrease, while the low-temperature properties deteriorate. Figure 5 exemplify this connection of acrylonitrile and low temperature performance by changing in T_g . This deterioration is due to, also, the amount of ACN content, since the T_g is determined by the configuration of the double bonds of the main chain, the number, size and polarity of the lateral groups [12]. Increasing the content of acrylonitrile, increases the polarity and so the T_g also increases. Additionally, nitrile rubber presents good abrasion properties, low compression set and low gas permeability.

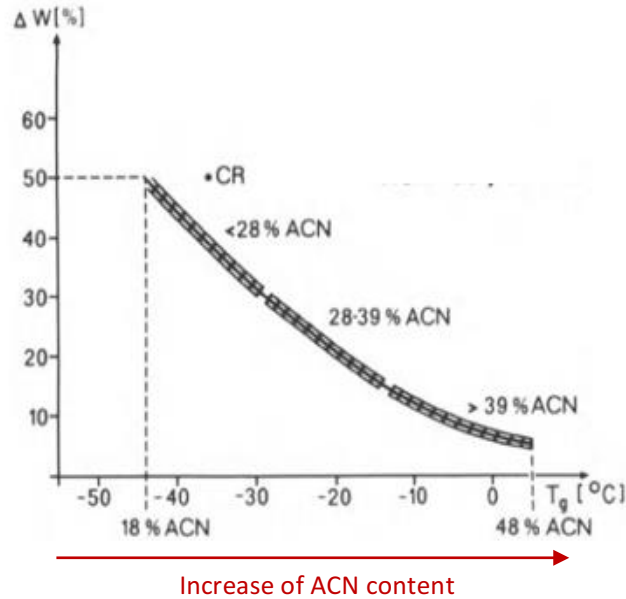


Figure 5 – Relationship between acrylonitrile (ACN) content, T_g and change of weight (ΔW) after immersion in ASTM oil No. 2. Adapted from [7].

Nitrile rubbers are resistant to water up to 70°C, air up to 100°C, fuels, mineral and vegetable oils. However, since NBR is a polar rubber, as mentioned above, it is not resistant to polar liquids such as chlorinated solvents, ketones, aldehydes, esters, nitrogen-containing solvents, air up to 150°C and hydraulic fluids (with exception of HFD type).

A study performed by Alves et al. [13] tested the resistance of NBR to diesel and biofuels (soybean, sunflower and palm biodiesel). Although it is well known that NBR presents good resistance to diesel, when it comes to biodiesel its performance decreases greatly. The swelling of nitrile rubber is substantially increased when immersed in biofuels, sometimes gaining 3.5 times its weight in mass.

The presence of double bonds in the elastomer backbone makes it susceptible to ozone and light. Sour gas wells and amine corrosion inhibitors also embrittle this elastomer. Due to the elevated level of unsaturation, NBR is subjected to oxidation and Sulphur attack [14].

HNBR withstands higher temperature, presents better resistance to swelling in technical fluids and chemical attack, specially of hydrogen sulfide and amine corrosion inhibitors, when compared to NBR. Higher levels of ACN promote better resistance to mineral oils while high levels of unsaturation lead to some sacrifice on the high temperature performance.

2.1.2 EPDM

EPDM is an elastomer based on ethylene and propylene monomers. The letter M, in accordance with ASTM D1418-17 nomenclature, indicates the class of elastomer with a methylene type saturated chain [7] while E stands for ethylene, P for propylene and D for diene. Figure 6 presents the chain representation of EPDM. This elastomer is a terpolymer developed after EPM (ethylene-propylene monomer). This improvement was motivated by the chemical saturation of EPM that impede the crosslinking by peroxide. EPDM presents less saturation than EPM and, then, can be crosslinked by peroxide and Sulphur based system. The ethylene-propylene elastomers are classified according to propylene and diene content by weight, usually between 25 and 55% and between 2 and 5% respectively [7]. Increasing the propylene content lead to softer and elastic rubber, while increasing the ethylene content improve the temperature resistance [7]. The ratio of the two monomers must be carefully chosen and controlled since it will directly affect the properties of the elastomer.

Regarding the temperature behavior of EPDM, it is well established that they are resistant to high temperatures. Service temperatures are usually up to 120°C but can reach 150°C depending on special composition. Peroxide cured EPDMs are more resistant to temperature than Sulphur cured. [4]

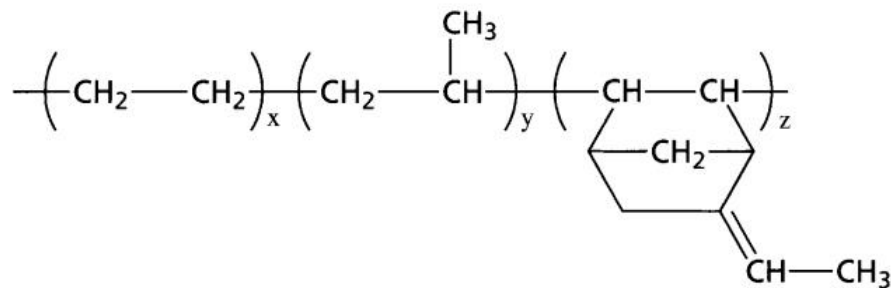


Figure 6 – Chain representation of EPDM

Mechanical properties

EPDM presents very good low temperature flexibility [6], which means that still presents elastic behavior until minimum temperature of -60°C [15]. The mechanical properties of the EPDM used in this study are presented on Table 2 and were provided by the supplier.

Table 2 – Mechanical properties of EPDM.

EPDM

Hardness	87 Shore A
Tensile Strength	2150 psi
Elongation	96 %

Chemical compatibility:

Ethylene-propylene rubbers present good resistance to ozone, water, oxygen, alkalis, hydraulic fluids. It is also resistant to low and high temperatures because of the completely saturated hydrocarbon backbones [7]. When increasing the content of ethylene, this type of elastomer becomes more stable at high temperature. The maximum service temperature is about 120°C, sometimes achieving 150°C for some grades. However, it shows fair to poor resistance to aliphatic, aromatic or chlorinated hydrocarbons [16], halogenated solvents, animal and vegetable oils.

As a general rule, EPDMs will not swell when in contact with highly polar liquids, but swelling may occur with aliphatic, non-polar or slightly polar liquids. Water, a highly polar liquid, is therefore not aggressive to EPDMs. However, it can cause swelling, albeit only slight, if the compounds contain low molecular weight water soluble substances. In this case, the water can enter to dissolve such substances. This must be taken into account when low water absorption is required at, for example, high temperature. [7].

According to Klingender [4], “all ethylene-propylene elastomers are sensitive to light and UV rays. If the vulcanized part is black, the carbon black it contains acts as an absorber, protecting items exposed to atmospheric agents and light for decades”. If the part is light colored, some other compounds may be added to increase the resistance to these factors. Usually, they are high purity paraffinic oil, zinc oxide (15-20 phr), rutile titanium oxide and phthalocyanine-based pigments.

2.1.3 FKM, FFKM and FEPM

Fluoroelastomers are used when good resistance to high temperature and very harsh environment are requested. They are generally dipolymers of VF₂ (vinylidene fluoride) and HFP (hexafluoropropylene) and the strong nature of the C-F bonds assess this resistance to fuel/oil and heat [17]. A third monomer, TFE (tetrafluoroethylene), may be

introduced to increase chemical resistance and most of times the addition of TFE lead to a reduction of VF₂ concentration.

The higher fluorine level lead to reduction of low-temperature flexibility due to increase of glass transition temperature. This effect can be compensated by the substitution of HFP by PMVE (perfluoromethylvinyl ether), which improves low-temperature performance but is a more expensive compound. However, the higher fluorine content improves chemical resistance of fluoroelastomers [18].

FKM is the designation of a vast family of fluoroelastomers of the polymethylene type, according to ASTM D1418, containing vinylidene fluoride as a monomer. It is based on hexafluoropropylene and vinylidene fluoride, and the grades available vary on the chemical building blocks used to polymerization. Figure 7 shows the representation of type I (VDF + HFP) and type 2 (VDF + HFP + TFE) FKM. The main variation between grades is on the level of fluorine content in the elastomer molecule, with higher contents leading to better resistance to chemicals and high temperature.

Some of the commercial names of FKM are Viton (developed by Dupont, nowadays sold for The Chemours Company) and Tecnoflon (by Solvay Solexis). Regarding minimum work temperatures, -20°C is the usual threshold for dynamic applications, although it may be even lower for static uses and vary according to the grade chosen. When it comes to cost, a comparison between FKM and Natural Rubber results in a relative cost of 40 times of NR's [19].

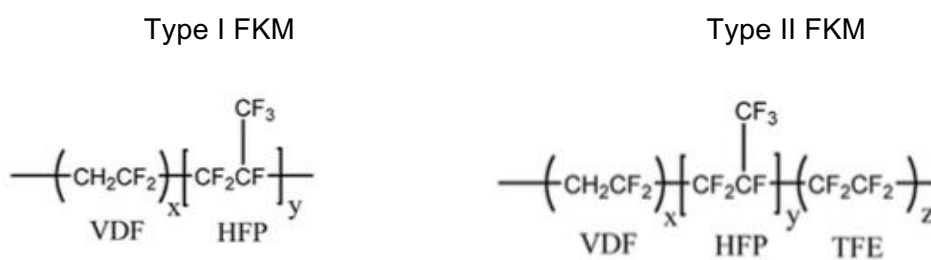


Figure 7 – FKM chain representation. (Adapted from Sugama et al., 2015)

There are some types of FFKM and they are differentiated by the monomers composition and curing system. According to ASTM D1418-17, it is a “perfluorinated rubber of the polymethylene type having all fluoro, perfluoroalkyl or perfluoroalkoxy substituent groups on the polymer chain”. The traditional FFKM is a copolymer of perfluoromethyl vinyl ether (PMVE) and tetrafluoroethylene (TFE) and its chain representation is presented on Figure 8 [6]. It presents the toughness of an elastomeric material with combination of the

outstanding chemical resistance of TFE. The monomers composition and sequencing during polymerization will significantly alter the low temperature behavior, whilst the curing system affects the chemical and thermal resistance.

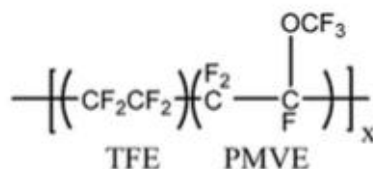


Figure 8 – FFKM chain representation (Adapted from [20])

FFKM presents extremely higher cost and more difficult processing compared to other elastomers. Some of the commercial names of FFKM are Kalrez, by DuPont, Tecnoflon PFR, by Solvay Solexis and Chemraz by Greene Tweed.

The traditional FFKM has Tg approximately 0°C, but it can be decreased by using other perfluorinated monomers, achieving values of -30°C for some grades. The addition of these monomers improved low-temperature properties and also maintain the chemical resistance of the elastomer. As mentioned above, one of the disadvantages of FFKM is the extremely high cost, achieving a relative cost of 1000 times the NR's price. [19]

FEPM is also designated as TFE/P, and its main commercial name is Aflas, by Asahi Glass. It is a copolymer of tetrafluorethylene and propylene, as shown in Figure 9 or a terpolymer of TFE, propylene and vinylidene fluoride. Aflas elastomers are divided in five categories, according to molecular weight and viscosity. The five categories present different mechanical properties and are directed to specific processing and applications but presents similar thermal and chemical resistance [14].

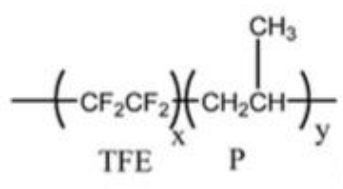


Figure 9 – TFE/P chain representation. (Adapted from [20])

When it comes to fillers and additives, non-reinforcing blacks and mineral fillers may be added to the compound to improve the processability, hardness and to reduce the cost. On the other hand, conventional plasticizers such as ester plasticizers are not compatible to this class of elastomer. For polymerization of FEPM, VF₂ is not used and this is the

key in achieving alkali resistance since vinylidene fluoride (VF₂) and hexafluoropropylene (HFP) sequence is prone to basic attack.

Mechanical properties

FKM exhibits great compression set and retained sealing force even at high temperature. This is one of the main factors FKM is desired when the combination of harsh environment and elevated temperatures is expected in the application.

The use of plasticizers in fluoroelastomers is, in general, not acceptable. However, some grades of elastomers have its low-temperature performance improved by the use of some plasticizers. In this case, if some plasticizer is added to the polymer, it will probably be exuded in service or in the post-cure treatment. According to Harper [14], fine-particle silica increases hardness, red iron oxides improves heat resistance and zinc oxide improves thermal conductivity.

FKM maintain its properties from -17°C (glass transition temperature) to 205°C, FFKM from -8°C to 315°C and FEPM from 0°C to 200°C [19]. It is important to highlight these values may vary from grade to grade, due to specificities of each supplier, blend and cure agent. The mechanical properties of FKM, FEPM and FFKM provided by the supplier are presented on Table 3.

Table 3 - Mechanical Properties of FKM, FEPM and FFKM.

	<i>FKM</i>	<i>FEPM</i>	<i>FFKM</i>
Hardness	93 Shore A	94 Shore A	78 Shore A
Tensile Strength	3030 psi	2100 psi	1609 psi
Elongation	95 %	67 %	119 %

Chemical compatibility

In general, fluoroelastomers exhibit excellent resistance to non-polar and nominally polar solvents, diesel, fuels, and oils. However, they are not resistant to solvents such as ketones and ester. The agent of cure used may lead to more specific chemical resistance [21]. For example, when steam and acid resistance are needed, the peroxide cured FKM presents better properties than bisphenol cured systems. When resistance to strong

alkalis are required, FEPM presents the best performance. FFKM, due to presence of TFE and even higher concentration of Fluor, resists to a large range of chemicals, even acid, ketones and alkalis. However, FFKM may be degraded by fully halogenated chlorofluorocarbons (CFC) and some fluorated solvents.

FKM have excellent resistance to oxidation, ozone, petroleum oils. They are also resistant to most mineral acids with high concentration and withstands service temperature up to 205°C, but this value may vary depending on the grade. However, caution when using alkalis and amines, especially at higher temperatures since this chemical may cause dehydrofluorination of FKM and this would lead to severe hardening and embitterment of the elastomer.

FEPM have excellent base resistance, such as amines and concentrated alkalis, and also bears higher work temperatures compared to FKM, generally up to 300°C. FFKM, due to the presence of TFE, resists to even higher temperature, achieving work temperatures such as 315°C. Also, it resists to corrosive chemicals, better than FKM. On the other hand, TFE/P generally presents poorer resistance to benzene and chlorinated solvent compared to conventional FKM. [6].

It is important to notice that exposing this class of elastomers to temperatures higher than the specified may lead to HF emissions.

2.2 Stress relaxation

Since elastomers are vastly used as seals, it is important to evaluate the behavior of the material against time when submitted to compressive stress. When compressed, the thickness of the material diminishes (even if, sometimes, this decay is very small). In field applications, sometimes occurs a relief in stress and the elastomer has to maintain the ability to return to its original shape (thickness) to guarantee the integrity of the seal and prevent any leakages [22]. This property of returning to original shape is the main attractive to use elastomers in sealing applications.

The capacity and time of recovery will vary depending on the contribution from the viscous and elastic characteristics of the elastomer compound. However, when deformed at high temperatures over time, the rubber material may not completely recover, but rather, will take on a permanent set. This is known as compression set (CS) as it measures the loss of shape memory [23]. In lower temperatures, this phenomenon can also occur but is generally reversible by heating and is usually called temporary set.

One way to evaluate the viscoelastic behavior is by compression stress relaxation (CSR) tests. The test consists in applying a constant strain to the material and evaluate the

variation (generally decay) of stress against time, as shown in Figure 10. This process of recovering shape is influenced by temperature, time and environment. Also, it can be physical or chemical, and under all normal conditions both processes will occur simultaneously. However, at normal or low temperatures and/or short durations, stress relaxation is dominated by physical processes; while at high temperatures and/or long durations, chemical processes are dominant [24].

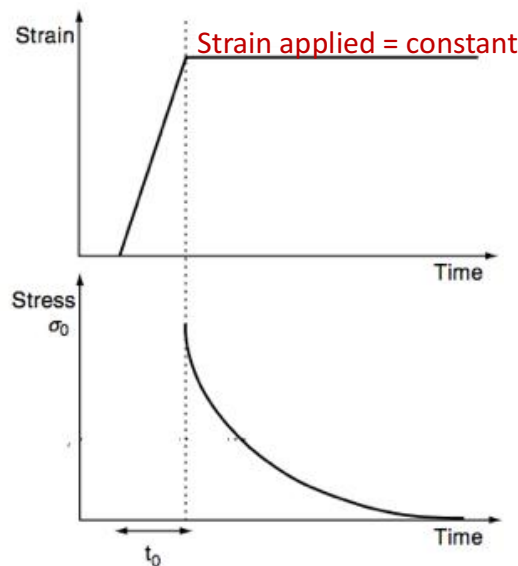


Figure 10 - Stress relaxation curves of strain and stress versus time, where t_0 and σ_0 are the initial time and stress, respectively. Adapted from [2].

The most common standards used to compression stress relaxation in elastomers are ASTM D6147 - Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomer—Determination of Force Decay (Stress Relaxation) in Compression and ISO 3384 – Rubber, Vulcanized or Thermoplastic: Determination of stress relaxation in compression. The test apparatus, sample and procedure defined in the standards will be discussed further in 3.4.

For lifetime prediction, it is necessary to develop a master curve that can correlate the mechanical property of interest (compression set, tensile strength, Young's Modulus) and time. As cited by RAPRA "the best known and most widely used model is the Arrhenius relationship which in particular is applied to the permanent effects of temperature as the degrading agent". Aiming the calculation for stress relaxation by Arrhenius, at least four different temperatures above the service temperature are chosen to perform the test [25] and, using established formulas and correlations, superimposing those curves to result in the above-cited master curve.

3 Materials and Methodology

3.1 Elastomers

In this study, six different rubbers were used. It is important to remember that only the chemical compatibility tests were performed with all rubbers, while the Compression Stress Relaxation (CSR) test were performed on just four types (HNBR, EPDM, FEPM and FKM). All elastomers were bought from Parker-Hannifin and the grade of each class of elastomer was acquired based on Oil & Gas application. The definition of the elastomers submitted to CSR tests was based on the immersion tests. Aiming at gathering information about all classes of elastomers, one of each group (nitrile, EPDM and fluorinated) was selected. Since literature presents few information regarding FEPM, it was decided to include this material in the CSR tests and, consequently, two fluorinated elastomers were tested.

All six rubbers arrived in sheets with dimensions 152.40 x 152.40 x 1.90 mm (6" x 6" x 0.075") in width, length and thickness respectively. The first step took after receiving the material was a visual inspection of the sheet integrity and the proper identification of the material. After that, the samples were cut in squares of, approximately, 28 x 28 mm for the immersion tests. The dimension was defined using the requirements of ISO 7619, suitability to the vessels used and to the scale's basket (to density measurements). Table 4 below presents the rubbers used by grade, supplier's specification, service temperature (from datasheet of the materials) and hardness (assessed in the laboratory).

Table 4 - Elastomers

<i>Elastomer</i>	<i>Supplier's specification</i>	<i>Hardness (assessed in laboratory)</i>	<i>Hardness (from supplier's datasheet)</i>	<i>Service temperature (from supplier's datasheet)</i>
NBR	N1059	90 Shore A	87 Shore A	-1°C to + 135°C
HNBR	KB163	90 Shore A	88 Shore A	-32°C to +149°C
EPDM	E0962	87 Shore A	87 Shore A	- 51°C to + 121°C
FEPM	VP103	93 Shore A	94 Shore A	-4°C to +232°C
FKM	V1238	90 Shore A	93 Shore A	-28°C to +204°C
FFKM	FF102	76 Shore A	78 Shore A	-15°C to +273°C

3.2 Fluids

At the total, five different immersion fluids were used to perform the chemical compatibility tests. Some of them are separated by application, given in its concentrated state and the chemical composition was not supplied (and could not be investigated by the NDA signed). Those chemicals are a Wax Inhibitor, a Demulsifier and an Asphaltene Inhibitor. Also, two solvents were used, and they are Diesel S-10 and Xylene. Moreover,

3.3 Chemical compatibility

The chemical compatibility tests were performed at room temperature (23°C) using all rubbers and five different fluids. The duration of the tests was 8 weeks. Samples were immersed and then withdrawn at the 1st, 2nd, 3rd, 4th and 8th week, three sample per withdrawn (triplicate), and they were not returned to the vessel. The quantity of samples per withdraw was defined as specified by ISO 1817: Rubber, vulcanized or thermoplastic — Determination of the effect of liquids 6th edition. The fluid of each vessel was replaced at each withdrawn, in order to keep the sample chemical composition. Due to the limited amount of fluid received, the Demulsifier and Diesel had the chemical compatibility tests reduced. For these fluids, only the 1st, 4th and 8th week withdraw was performed.

The definition of size of the samples followed the ISO 1817 and ISO 7619:2010 - Rubber, vulcanized or thermoplastic — Determination of indentation hardness — Part 1: Durometer method (Shore hardness), which can be seen on Table 5.

Table 5 – Sample dimension

Geometry	Thickness (mm)	Width (mm)	Length (mm)	Estimated volume (ml)
Square (2D)	1.9	28	28	1.4896

3.3.1 Immersion

A glass vessel of approximately 1200 mL of volume was used for the immersion test. The vessel set consists of a glass jar, an O-ring for sealing the cap, a glass lid and an aluminum cap tightener. These components and the vessel assembled are presented in Figure 11.



Figure 11 – Vessel components (left) and vessel assembled (right)

Before the beginning of the tests, the vessels were tested against leakage. The test consists of filling the vessel with water and turning it upside down on a paper towel, as presented in Figure 12. The vessel remains in this position for 7 days and checked every hour. If the paper towel remains absolutely dry at the end of this period, the vessel is considered as leak-proof.



Figure 12 – Immersion vessel assembled during leakage test

The chemical compatibility tests followed ISO 7620. The samples were placed in glass holders to assure that all its surface was in contact with the fluid. The amount (volume) of fluid used in each vessel was defined as specified in ISO 1817, being at least 15 times the combined volume of the test pieces. The minimum amount of fluid per vessel is presented on Table 6 based on those requirements of ISO 1817 and the theoretical calculation of volume of each sample.

Table 6 – Estimative of fluid amount per vessel

Volume of each sample (ml)	Amount of sample per vessel	Combined volume of test pieces (ml)	Minimum volume of fluid (ml)
1.5	20	30	15 x 30 = 450

Due to the toxicity of the fluids and in accordance with the HSE practices, all personnel involved with the handling of the chemicals was properly equipped with individual protective equipment (IPE). It consists of a long-sleeve lab-coat, gloves, special protective glasses and masks against organic volatiles.

3.3.2 Mass and volume variation

The mass and volume of the samples were measured before the beginning of the tests (unaged samples) and after each withdrawal. The same scale was used from the very first time until the last measurement to minimize the source of errors on the values. The precision of the scale is $\pm 0.0001\text{g}$, compliant with the specified by ISO 1817. Each sample was weighted five times and the mass variation of the sample is the average of these measurements. For each rubber, as specified before, three samples were retrieved at each time interval. The results of mass variation for each class of rubber tested will be presented as the average of the three samples variation. The mass variation is calculated as Equation 1.

$$\Delta m(\%) = \frac{m_i - m_0}{m_0} \times 100 \quad (1)$$

Where:

m_0 = initial mass (unaged sample)

m_i = mass after time t_i

Regarding volume variation, it was measured in the same scale using an Archimedes accessory. The accessory is coupled to the scale and is constituted of a becker filled with distilled water and a basket where the sample is placed. In this stage, it is important to assure that no bubbles are formed on the sample's surface and that the time is not long enough to cause water absorption, so the results are as accurate as possible. When placing the sample inside the basket, it occurs a water displacement that gives the parameters that allows the calculus of volume. If some of the test pieces presents a density lower than water's, then a sinker needs to be used to guarantee that the samples

is completely under water. In this case, the sinker will also be weighted in air and inside water to complete the equation. Finally, to calculate the volume, it is used the mass in air (m_0 , m_i) and the mass in water ($w_{0,w}$, $m_{i,w}$). The Equation 2 used for the volume variation calculus and is presented below.

$$\Delta V (\%) = \left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100 \quad (\text{Equation 2})$$

Where:

m_0 = initial mass of the test piece in air;

m_i = mass of the test piece after immersion in air;

$m_{0,w}$ = initial mass of the test piece (plus sinker if used) in distilled water;

$m_{i,w}$ = mass of the test piece (plus sinker if used) after immersion in distilled water;

$m_{s,w}$ = mass of the sinker, if used, in distilled water.

The result reported is presented as the average of the three test pieces.

3.3.3 Shore Hardness

The hardness was measured according to ISO 7619:2010. The standard requires that the test pieces are least 6mm thick. As an alternative, if the samples do not achieve that value, until three pieces can be stacked. Since the rubbers received are 1.9mm thick, approximately, even plying three samples it is not possible to achieve the minimum value required. However, for means of comparison and evaluation of degradation, the hardness was still measured for unaged and aged samples. Also, the hardness of the unaged samples was measured and these values were used in the comparison, preserving the accuracy of the results.

The test procedure consists in

The laboratory possesses two types of durometers for Shore scale, type A and type D. The type A is used for softer rubbers, while type D is used for stiffer rubbers. If using type D Shore scale the hardness value is lower than 20, type A scale shall be used instead. Figure 14 shows an illustrated scheme of the coverage of Shore A and Shore D. Moreover, if using type A scale the values are higher than 90 Shore A, type D shall be used.

Figure 13 presents the apparatus used for the measurements.



Figure 13 – Shore A hardness apparatus

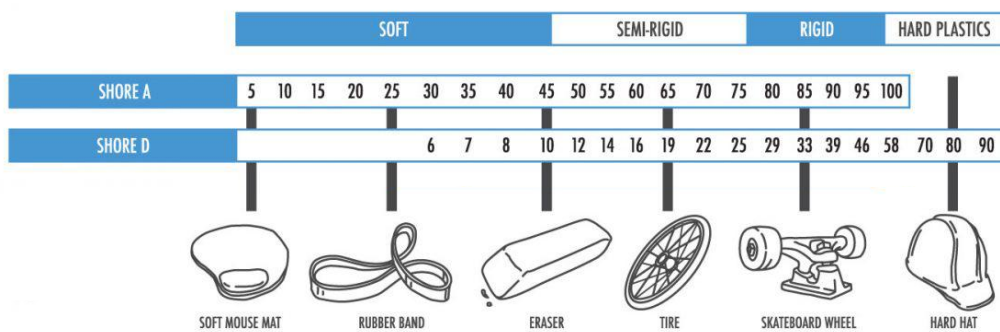


Figure 14 – Shore hardness scale. Adapted from [26]

The test procedure consists in placing the plied-up test pieces on a leveled, flat, hard and rigid glass surface. Then, the pressure foot is slowly pressed on the test piece surface ensuring that the indenter is normal to the rubber surface. The hardness reading is made after 3 seconds, standard time for vulcanized elastomers.

ISO 7619:2010 also specifies that the indentation shall be made at least 12mm apart from each edge, and the distance between the measurements shall be at least 6mm. From that, it was specified the region of the rubbers where the test shall be performed, and a scheme is presented below on Figure 15.

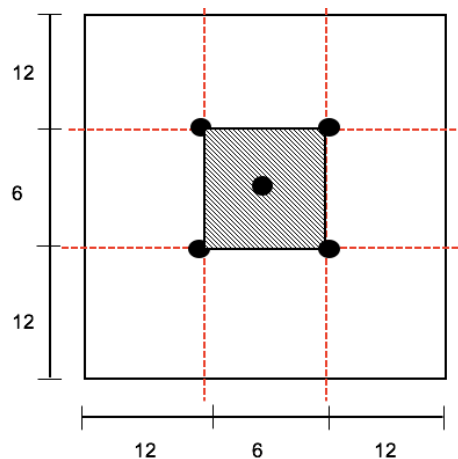


Figure 15 - Test piece scheme. The hatched square represents the eligible area where the hardness indentation can take place

3.3.4 Post-immersion tests

The post-immersion tests were only performed in the 8-week aged samples in Xylene. It consists in measuring mass, volume and hardness after 45 days, time span assumed to allow the evaporation of the solvent. These measurements followed the same procedure specified in 3.3.2 and 3.3.3.

3.3.5 FTIR

FTIR stands for Fourier Transform Infrared Spectroscopy, which is a technique for evaluation of the composition of some material. The operation of the equipment is based on an emission of an infrared radiation through the material. This radiation may pass through (be transmitted) or be absorbed by the sample. In the latter case, it is converted into vibrational or rotational energy by the material's molecules and is characteristic of a specific chemical bond. From this data, the instrument generates a spectrum of wave number (reciprocal of the wave length and proportional to the frequency of the radiation) and of the percentage transmission (T) or absorbance (A), as related to the energy of the radiation [27].

The FTIR analysis was performed on samples aged in Xylene for 1, 4 and 8 weeks, after the evaporation of the solvent (45 days). The objective of waiting until evaporation of Xylene before performing FTIR was to evaluate the actual effect of the fluid in the elastomer chain. If the analysis were performed right after the retrieval of the samples from the immersion vessels, some peaks referred to the fluids would appear and probably this would have mascaeraed the peaks relative to the rubber bonds

One unaged sample of each elastomer was also characterized to use as reference. It was expected to identify the modifications that the fluids induced in the chemical structure of the rubbers and use these data to underlie the variation of mass, volume, hardness and compression stress relaxation behavior. However, due to the presence of carbon black in the elastomers that absorbs and scatters radiation [28], the spectra obtained was not so neat as expected. Figure 16 below schematizes the influence of carbon black on the FTIR spectra of an SBR sample.

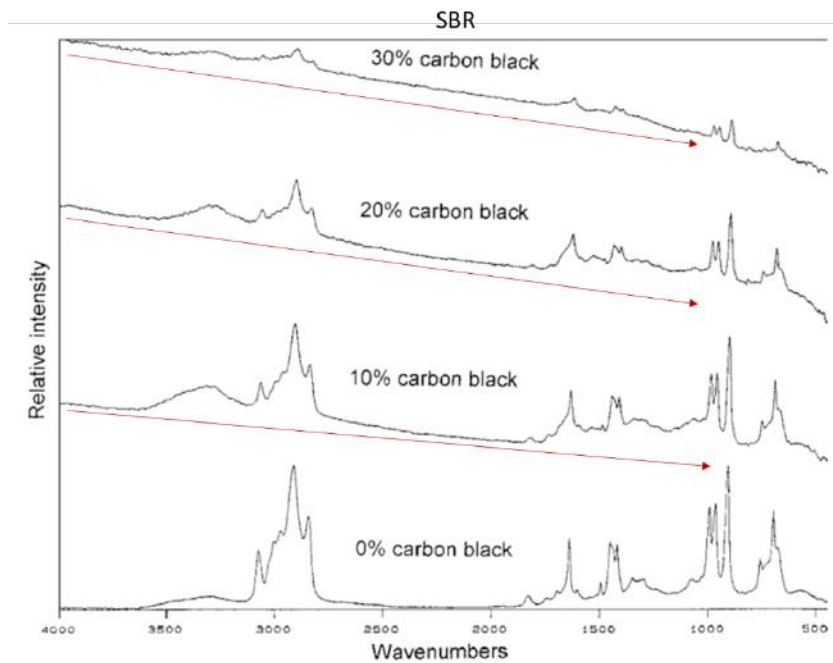


Figure 16 – Effect of carbon black on PA-FTIR spectrum of styrene-butadiene rubber (SBR). Adapted from [28].

3.4 Stress relaxation test

The Compression Stress Relaxation (CSR) tests were performed on an electro-mechanic testing machine (Instron 5567). A load cell of 10 kN was selected for the tests based on pre-tests performed on each rubber. This pre-test consists in, basically, compressing the rubber until it shows, at least, 30% of deformation. From the results of the pre-test, the necessary load to achieve a 25% strain is defined and this allows the selection of the most suitable load cell. Although it would be possible to use load cells of greater magnitudes, the selection also involves achieving the best precision possible. This test precision, regarding the load, is 1/283 of the load cell value. In this case, the precision is ± 35.34 N, in accordance with ASTM D6147 which requires a precision of, at least, $\pm 1\%$. Also, it is important to highlight that the load cell chosen was the best suitable for all rubbers tested.

The ASTM D6147 was used as a guide line for the test procedure. Regarding the test period, it stands that “the duration of the test shall be mutually agreed upon by the customer and the supplier”. Moreover, ISO 3384, an equivalent standard for CSR tests, indicates that intermediate times of 3, 6, 24 and 72h are preferred if a long-term test of 168h could not be performed. Based in those suggestions and considering the availability of the equipment, a period of 180 minutes was defined for the CSR tests.

Regarding the test, ASTM D 6147 stands that the initial 25% load shall be applied in a time interval of 30 seconds. Since the rubbers did not present the same thickness, the load rate applied varied among them, always in accordance with ASTM procedure. At this point, it is important to say that a pre-load of 1.0 N, at a rate 1N/min, was also applied to assure the contact of the rubber and the compression jigs. Although this procedure was not specified by neither ASTM nor ISO, it was included based on previous tests that lead to inaccurate results when not pre-loaded.

Since the objective of the tests is to simply compare the behavior of the aged and the unaged samples, it was agreed that maintaining the same procedure for all tests, the results would be accurate to compare them. It is not possible, though, to compare the results from tests following different procedures. Also, the initial deformation caused by the pre-load was taken into consideration when calculating the load rate for the CSR tests. Equation 3 below exemplifies the calculus for each test.

X_i = initial thickness

def = % deformation due to pre-load

x_{CSR} = deformation defined for the test, i.e., 25 %

$$x_{CSR} = 0,25 \cdot X_i$$

$$x_{residual} = x_{CSR} - def \cdot X_i$$

$$\text{rate (strain/min)} = \frac{x_{residual}}{30} \cdot 60 = 2 \cdot x_{residual} \quad (\text{Equation 3})$$

The test specimen was stamped from the rubbers sheets, for the unaged samples, and from the coupons used in the chemical compatibility tests for the aged samples. All of them were discs of 13mm, and the thickness varied from 1.79 to 2.17. Figure 17 shows the coupons from where the discs were stamped and the disc used on the CSR tests. ASTM D6147 proposes three different geometries for the test that did not match with ours. However, ASTM also stands that “other test specimen sizes may be used as dictated by end use”. Since the chemical compatibility tests were performed with samples within the above cited range of thickness, it was decided to perform the CSR tests with the same dimensions. The results of the immersion tests are directly related with the

thickness of the samples, and the evaluation of the effects of the fluids on the mechanical behavior would be more accurate maintaining the same geometry.

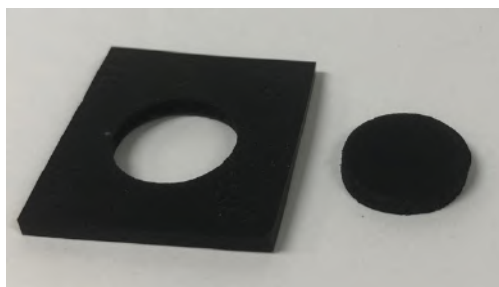


Figure 17- Immersion test sample (left) from where the CSR test specimen was stamped (right)

Due to the elevated combination of conditions, it was not possible to do stress relaxation tests with all rubbers after each withdrawn neither with all test combinations of rubber and fluid. This test was performed with HNBR, EPDM, FEPM and FKM in the conditions “unaged” and aged for 8 weeks in Xylene. The stress relaxation was monitored for 180 minutes. The materials were chosen based on the immersion test’s results. Xylene was the most aggressive fluid for all rubbers and the above-cited elastomers were the most affected.

Although NBR presented was also great swelling when immersed in Xylene, the results were very similar to HNBR and, then, it was decided to test only HNBR. FEPM was chosen based on its also good results but, mainly, due to lack of information available regarding this material. EPDM, on the other hand, was chosen because was the most affected by Xylene and it would be interesting to evaluate how the fluid affect the mechanical properties of this rubber.

4 Results

The results will be exposed in this chapter, separated by rubber and divided into 4 topics: immersion tests, post-immersion tests, compression stress relaxation (when applicable) and FTIR. Due to similarity of results and rubbers of the same class, the discussion will be presented in Chapter 5 separated by those classes, following the same structure as Chapter 2.

The immersion tests had a total duration of 8 weeks. However, it is important to highlight that, as specified in Chapter 3.3, the immersion in Diesel using NBR, HNBR and FKM and for the immersion of all rubbers in Demulsifier were reduced and only three withdraws were performed.

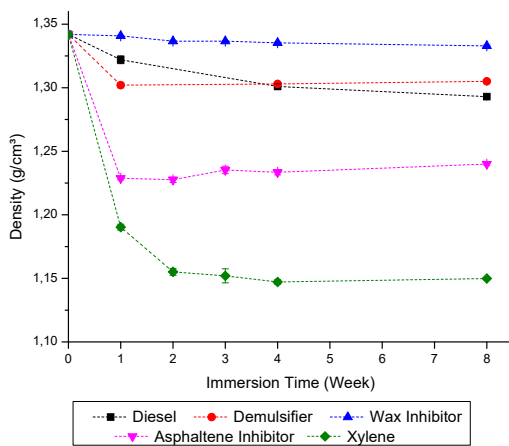
Regarding the hardness results, some small variation is expected due to the characteristics of the tests. The hardness measurements, although standardized, are very sensitive to the velocity of pulling the indenter's handle. Also, when the indicator stands between two hardness values, it is necessary to round (up or down) the value since only whole numbers are accepted.

It is important to highlight that regarding the Compression Stress Relaxation curves, the Y-scale was maintained the same for all curves presented aiming at better comparison of results. The range for Y-scale was from 0.5 to 1, so all the curves, of all rubbers tested, could fit in the interval.

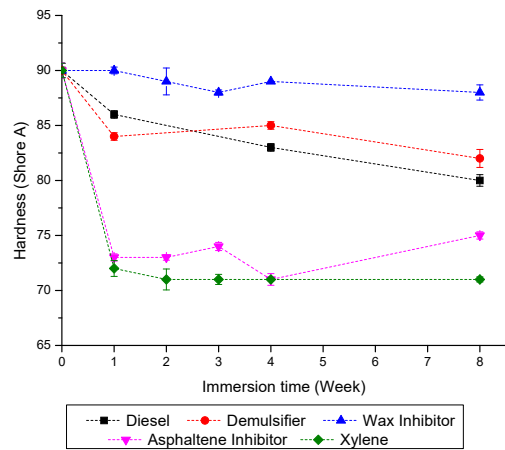
4.1 NBR

4.1.1 Immersion tests

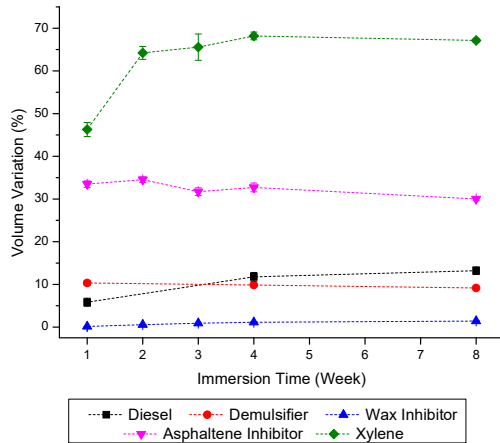
The results of density, hardness, mass and volume variation are presented in Figure 18. The error bars represent the standard deviation. The mass and volume curves present the same configuration, which could also give the impression that the mass variation curve is a duplicate of volume variation. However, the curves are accurate and present this particular behavior of following the exact same tendency.



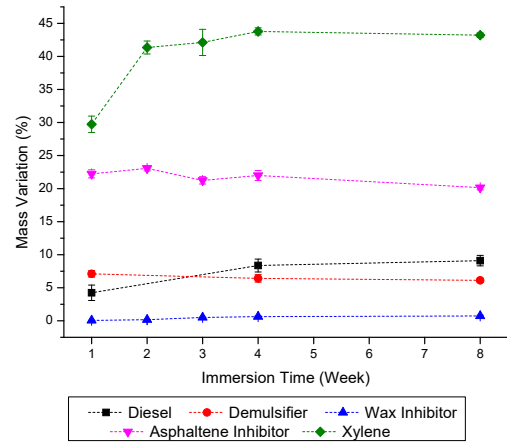
(a)



(b)



(c)



(d)

Figure 18 – (a) Density, (b) Hardness, (c) Volume and (d) Mass variation of NBR immersed in all fluids for 8 weeks.

Figure 19 and Figure 20 show the immersion vessels before (just after the assembly) and after 1 week of immersion in Diesel and Xylene respectively.



Figure 19 – Immersion vessel of NBR in Diesel (a) before immersion (B) after 1 week of immersion



Figure 20 – Immersion vessel of NBR in Xylene (a) before and (b) after 1 week of immersion

4.1.2 Post-immersion tests

The results of mass, volume and hardness measurement after evaporation of NBR immersed in Xylene for 8 weeks are presented in Table 7. The initial values of mass and volume are not presented because the results after immersion and evaporation are shown as a percentage of the initial values.

Table 7 – NBR mass, volume, density and hardness variation of 8 week aged samples in Xylene just after immersion and after evaporation.

NBR in Xylene (8 weeks of immersion)

	Initial	After immersion	After evaporation
Mass variation (%)	N/A	43.22 ± 0.34	- 5.34 ± 0.04
Volume variation (%)	N/A	67.15 ± 0.50	- 7.14 ± 0.15
Density (g/cm³)	1.342	1.150 ± 0.001	1.368 ± 0.02
Hardness (Shore A)	90	71	90

4.1.3 FTIR

Figure 21 presents the FTIR spectra for NBR in the condition as-received and aged after 1, 4 and 8 weeks in Xylene. No difference could be observed between the spectra.

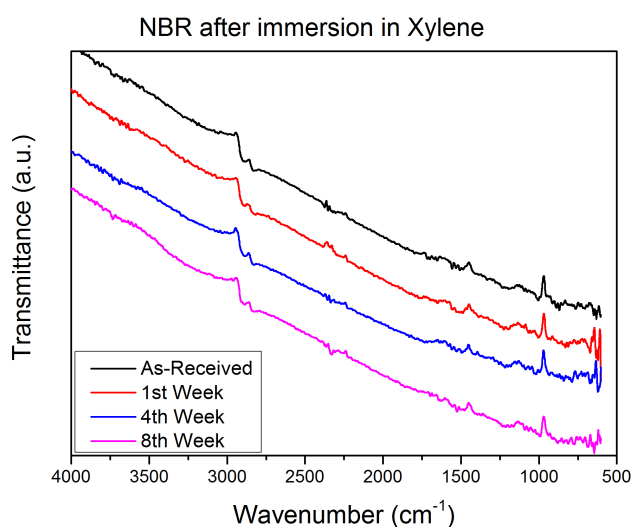


Figure 21 – FTIR curves of NBR in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene.

4.2 HNBR

4.2.1 Immersion Tests

The results of density, hardness, volume and mass variation of all immersion tests are presented in Figure 22.

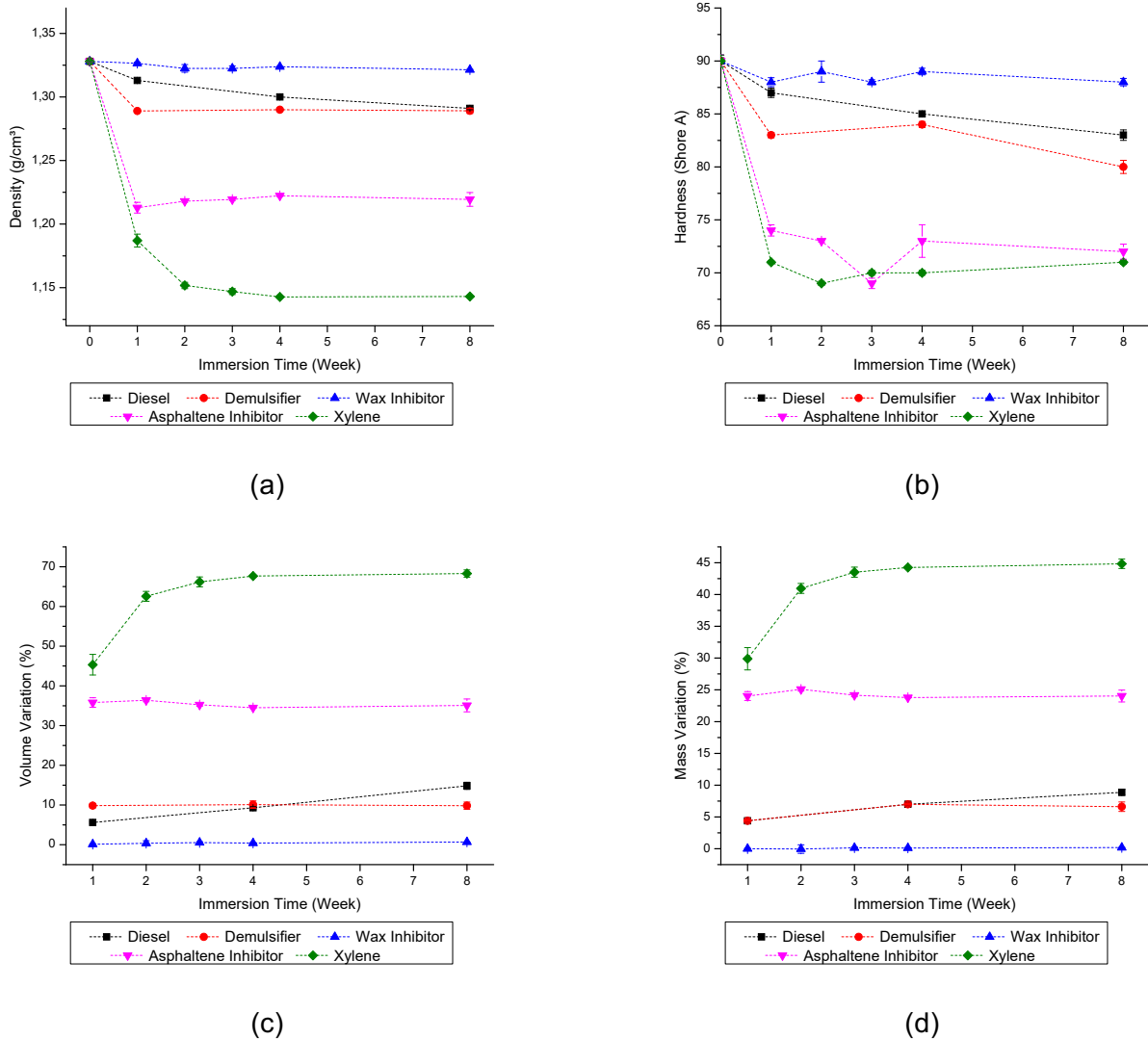
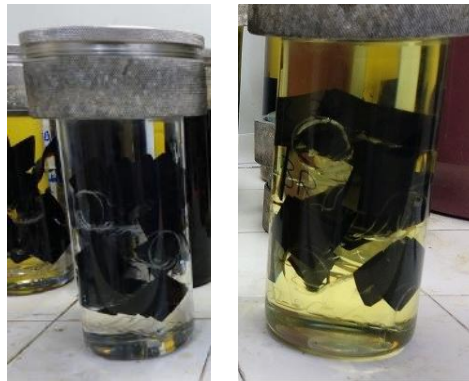


Figure 22 – (a) Density, (b) Hardness, (c) Volume and (d) Mass variation of HNBR immersed in all fluids for 8 weeks.

Figure 25 and Figure 24 show the immersion vessels just after the assembly of the test and after 1 week of immersion in Diesel and Xylene respectively.



Figure 23 - Immersion vessel of HNBR (a) before and (b) after 1 week of immersion in Diesel



(a) (b)

Figure 24 – immersion vessels of HNBR (a) before and (b) after 1 week of immersion in Xylene

4.2.2 Post immersion tests

Table 8 presents the comparative data of mass, volume density and hardness after immersion in Xylene and after evaporation. Since the mass and volume data are presented in percentage of initial (unaged) value, the values in these columns are presented as “N/A”, which stands for “not applicable”. The hardness after evaporation returns to the same value as the unaged condition. Mass and volume show a slight decrease. The density after evaporation is slightly higher than the unaged sample (1.335 and 1.328 g/cm³ respectively), but this variation is only 0.5% of the original value.

Table 8 – Mass, volume, density and hardness variation of HNBR after immersion in Xylene and after evaporation.

HNBR in Xylene (8 weeks immersion)

	Initial *	After immersion	After evaporation
Mass variation (%)	N/A	44.84 ± 0.74	- 1.96 ± 0.01
Volume variation (%)	N/A	68.28 ± 0.92	- 2.50 ± 0.01
Density	1.328	1.143 ± 0.001	1.335 ± 0.001
Hardness (Shore A)	90	71	90

4.2.3 FTIR

The FTIR spectra of HNBR unaged and aged for 1, 4 and 8 weeks in Xylene is presented below in Figure 22. No differences between the aged samples' spectra and the unaged's could be observed.

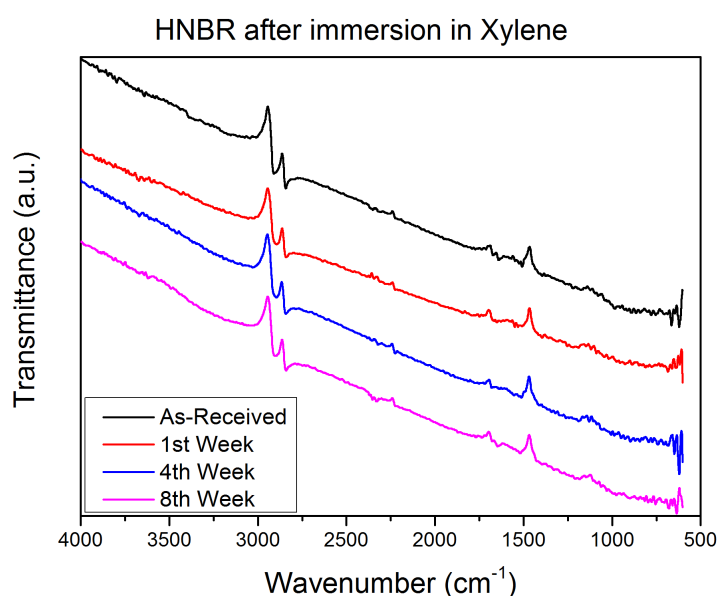


Figure 25 - FTIR curves of HNBR in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene

4.2.4 Compression Stress Relaxation

Figure 26 shows the compression stress relaxation curves for HNBR unaged and aged in Xylene for eight weeks. It is possible to observe that the ageing did not altered the behavior of the rubber under compression stress relaxation.

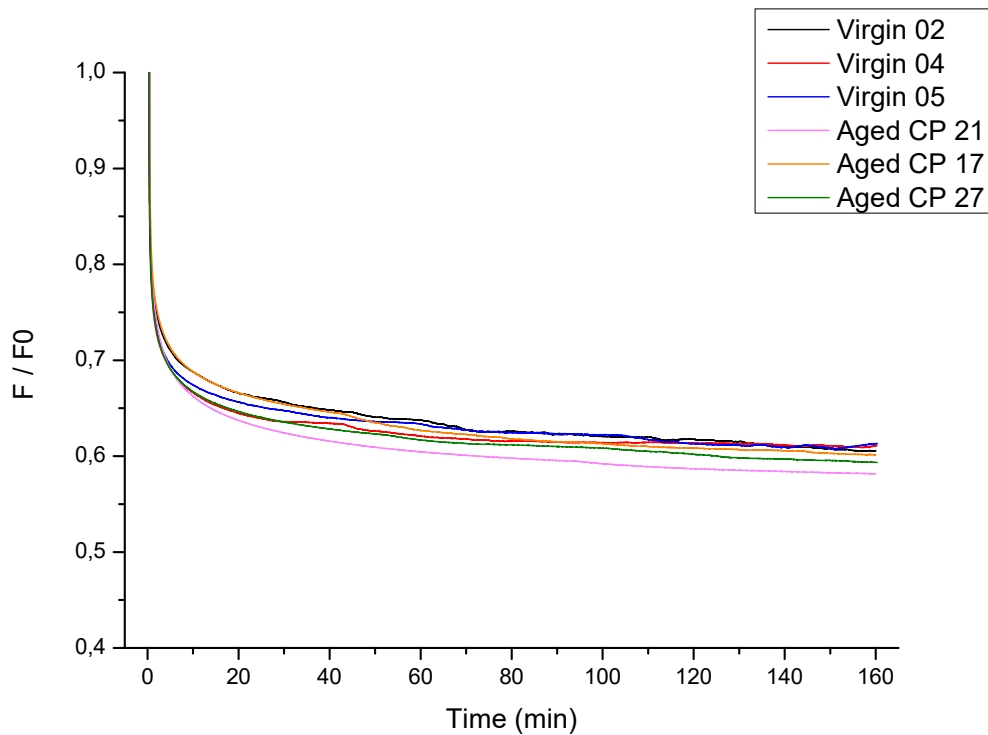
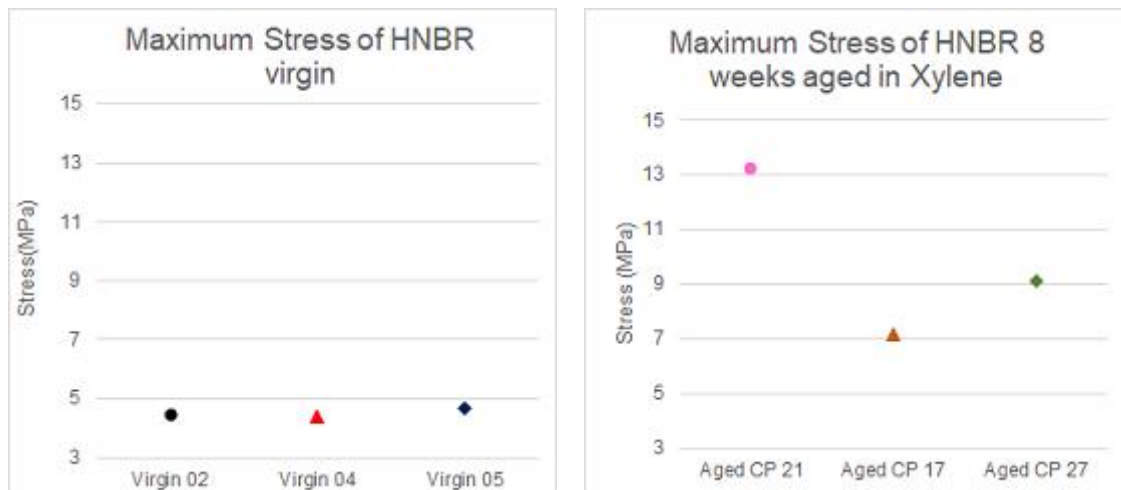


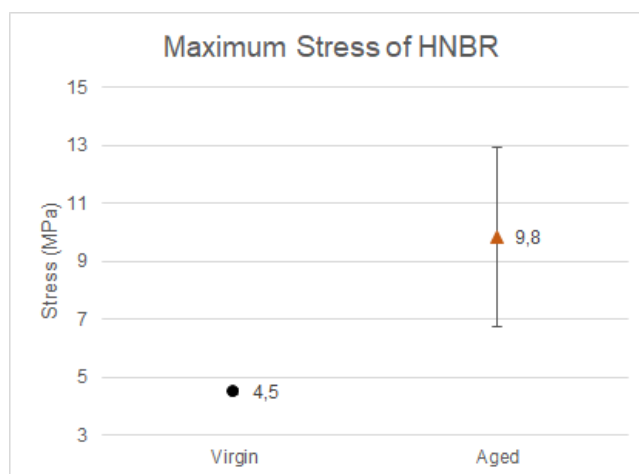
Figure 26 - Compression Stress Relaxation curves of HNBR Unaged and 8 week aged in Xylene

Figure 27 a, b and c show the maximum stress achieved for each of the unaged samples, each of the aged samples and the average of each condition with standard deviation, respectively.



(a)

(b)



(c)

Figure 27 – Maximum stress of HNBR (a) unaged, (b) aged and (c) average of both conditions

4.3 EPDM

4.3.1 Immersion tests

The results of density, hardness, mass and volume variation of the immersion tests are presented in Figure 28.

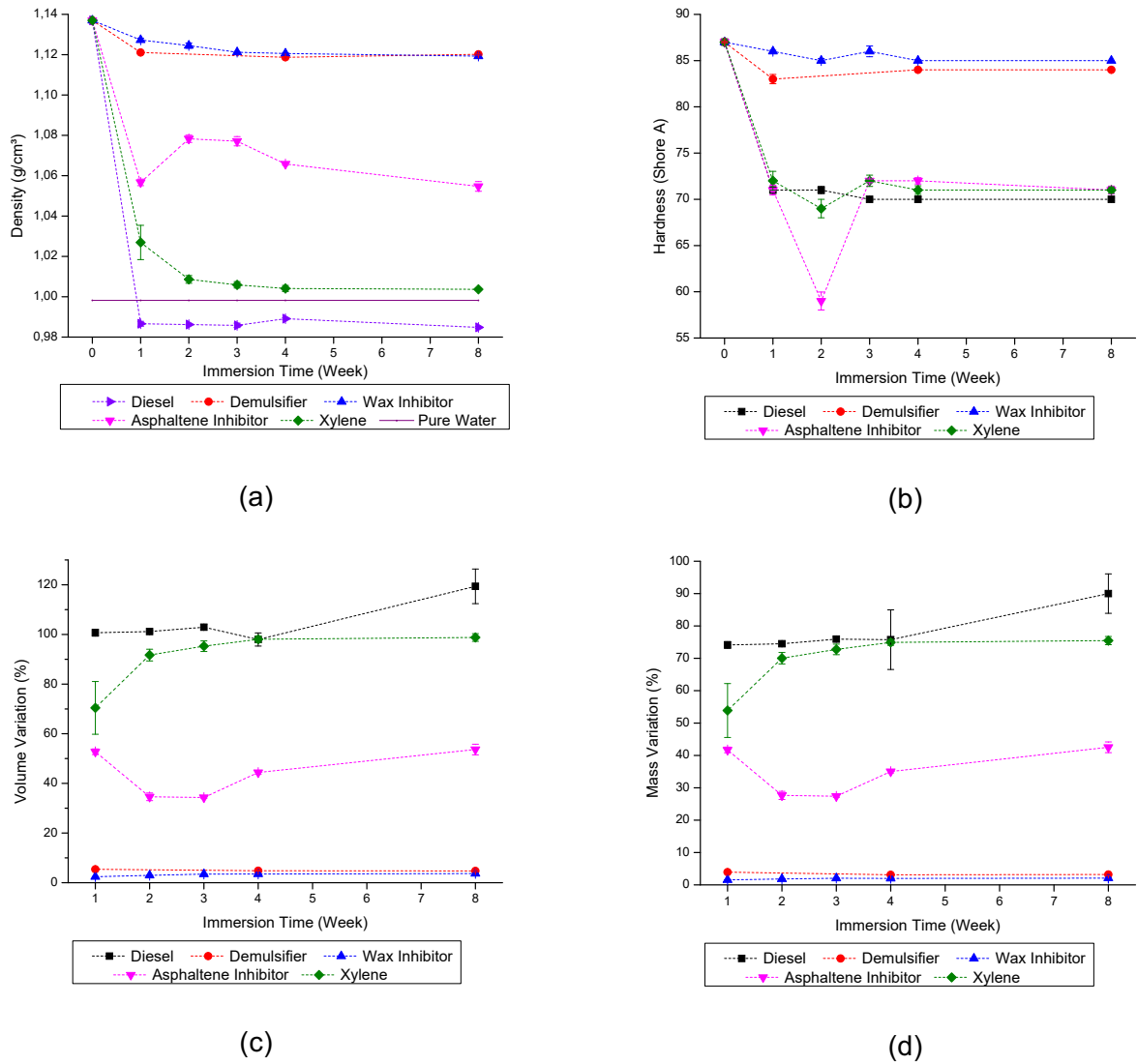


Figure 28 – (a) Density, (b) Hardness, (c) Volume and (d) Mass variation of EPDM immersed in all fluids for 8 weeks.

4.3.2 Post-immersion test

The post-immersion tests results of EPDM are presented below on Table 9. The data of mass and volume are presented as percentage of initial mass, so no data of the initial values are presented. For this reason, these cells are presented as “not applicable” (N/A).

Table 9 – Post-immersion results of EPDM aged in Xylene for 8 weeks

EPDM in Xylene (8 weeks of immersion)

	Initial *	After immersion	After evaporation
Mass variation (%)	N/A	75.45 ± 1.26	- 1.86 ± 0.10
Volume variation (%)	N/A	98.78 ± 1.56	- 2.72 ± 0.05
Density	1.137	1.004 ± 0.001	1.147 ± 0.002
Hardness (Shore A)	87	71	87

4.3.3 FTIR

Figure 29 shows the FTIR spectra of EPDM in the as-received condition and after immersion in Xylene. No differences could be seen between the aged and the unaged's spectra.

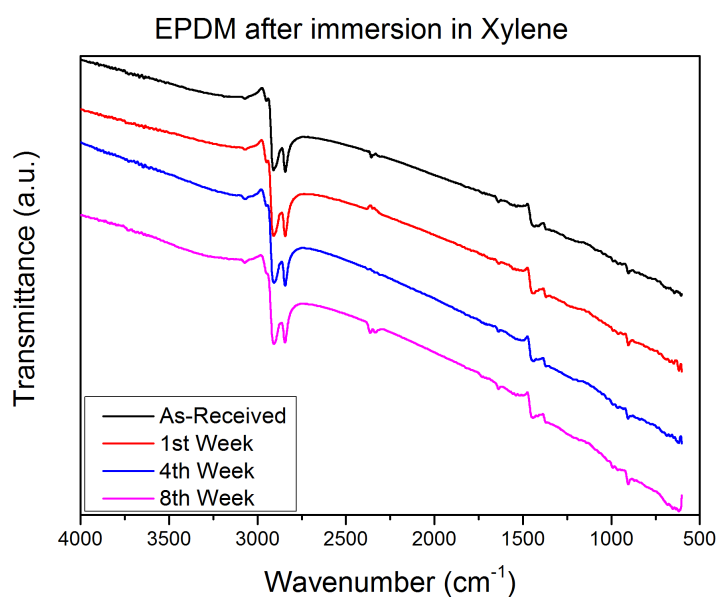


Figure 29 - FTIR curves of EPDM in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene

4.3.4 Compression Stress Relaxation

Figure 30 shows the compression stress relaxation curves of EPDM unaged and aged in Xylene for 8 weeks.

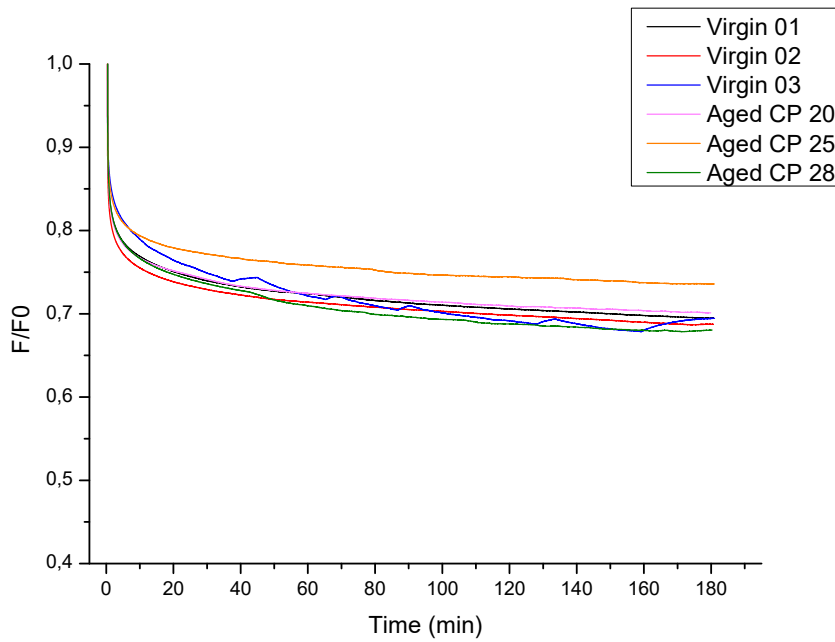
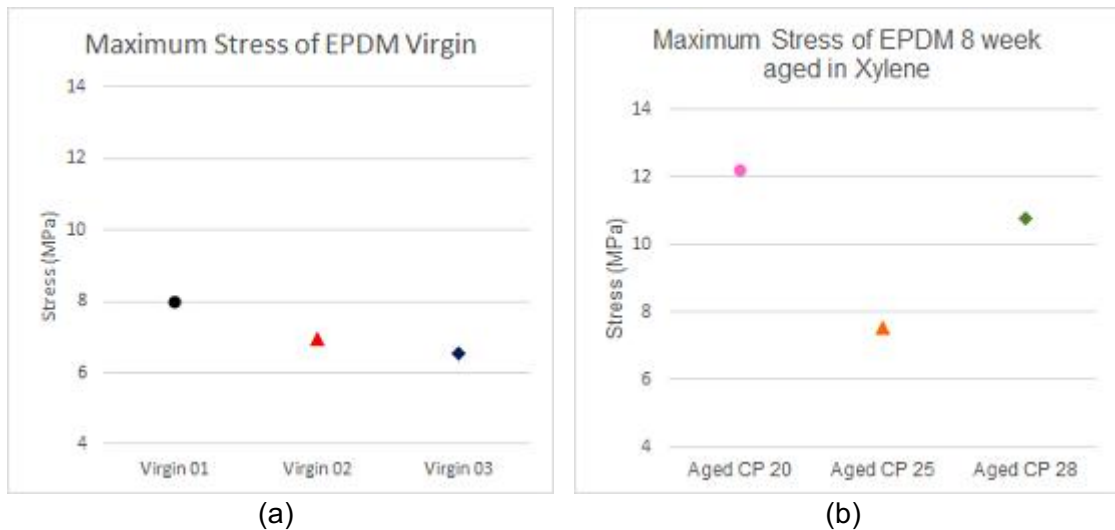
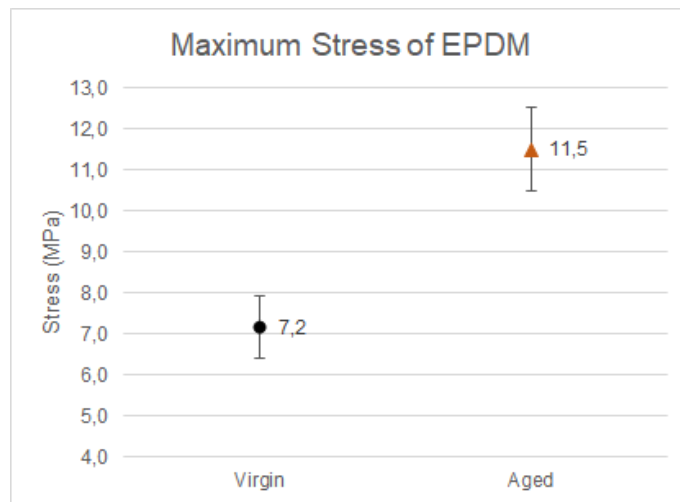


Figure 30 – Compression Stress Relaxation curves of EPDM unaged and 8week aged in Xylene

Figure 31 a, b and c show the F₀, namely the maximum stress achieved in CSR tests, of EPDM unaged, aged and a comparison of the average of both conditions, respectively.





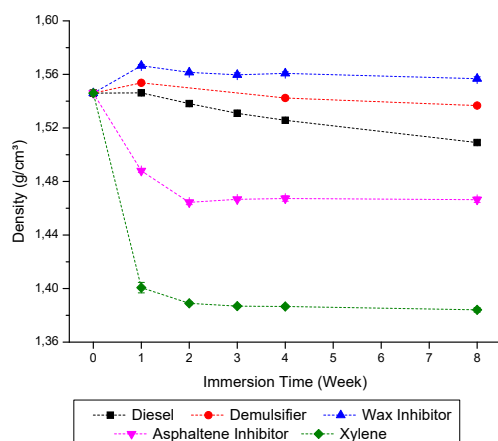
(c)

Figure 31 – Maximum stress (F_0) of EPDM (a) unaged, (b) aged, (c) average of both conditions

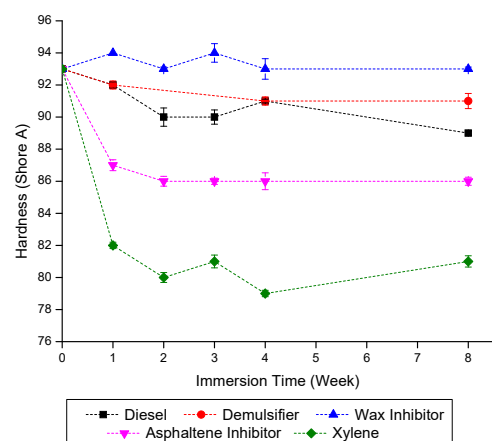
4.4 FEPM

4.4.1 Immersion tests

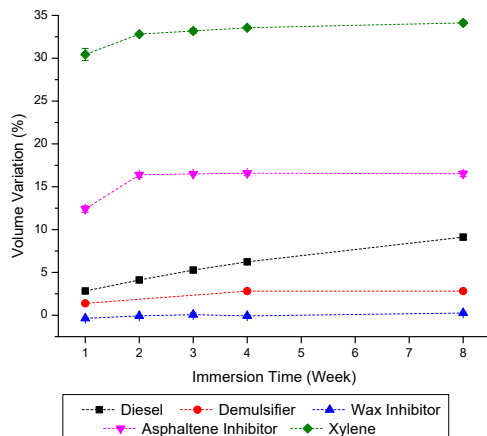
Figure 32 shows the results of mass, volume, density and hardness variation of FEPM immersed in all fluids.



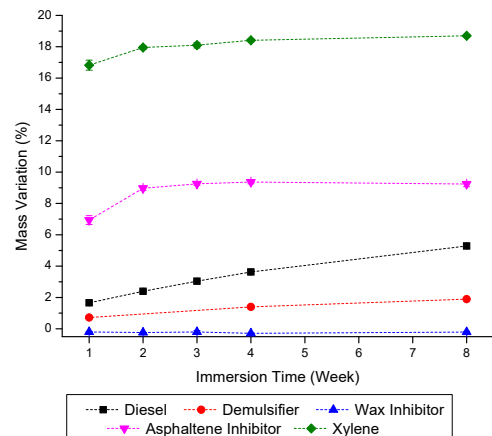
(a)



(b)



(c)



(d)

Figure 32 - (a) Density, (b) Hardness, (c) Volume and (d) Mass variation of FEPM immersed in all fluids for 8 weeks.

4.4.2 Post-immersion tests

The results of the post-immersion tests of FEPM aged for 8 weeks in Xylene are presented in Table 10. “N/A” stands for “not applicable”.

Table 10 – Post-immersion results of FEPM

FEPM in Xylene (8 weeks immersion)

	Initial *	After immersion	After evaporation
Mass variation (%)	N/A	18.70 ± 0.08	- 0.22 ± 0.03
Volume variation (%)	N/A	34.12 ± 0.26	-0.26 ± 0.13
Density	1.564	1.384 ± 0.002	1.563 ± 0.005
Hardness (Shore A)	93	81	93

4.4.3 FTIR

Figure 33 shows the FTIR spectra of FEPM as-received and aged for 1, 4 and 8 weeks in Xylene.

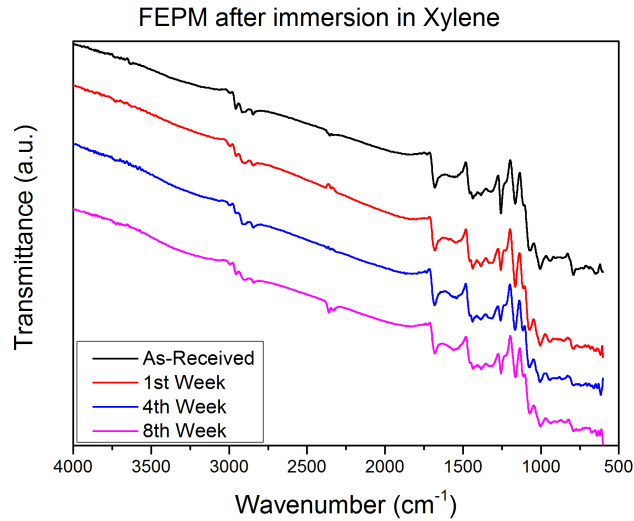


Figure 33 - FTIR curves of FEPM in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene

4.4.4 Compression stress relaxation

Figure 34 shows the compression stress relaxation curves of FEPM unaged and aged in Xylene for 8 weeks.

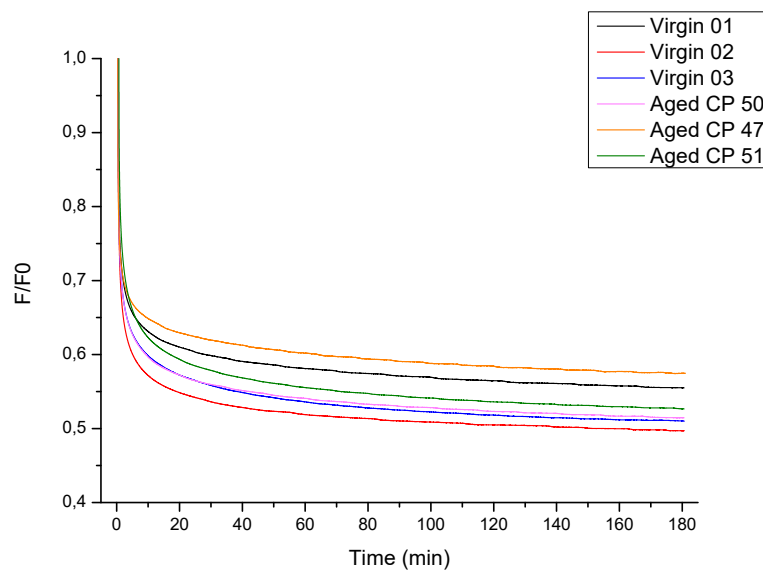
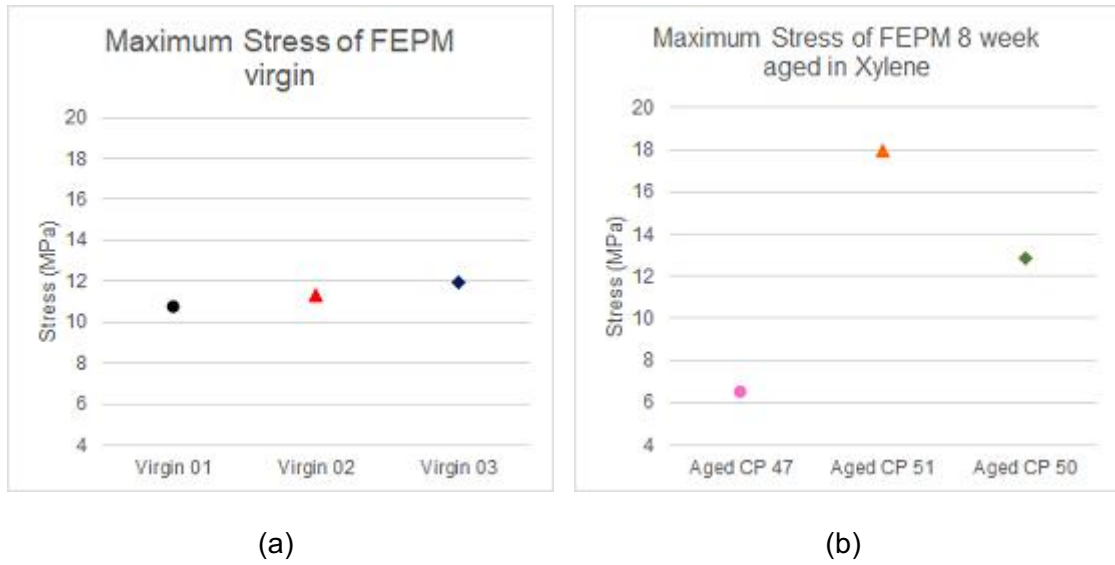


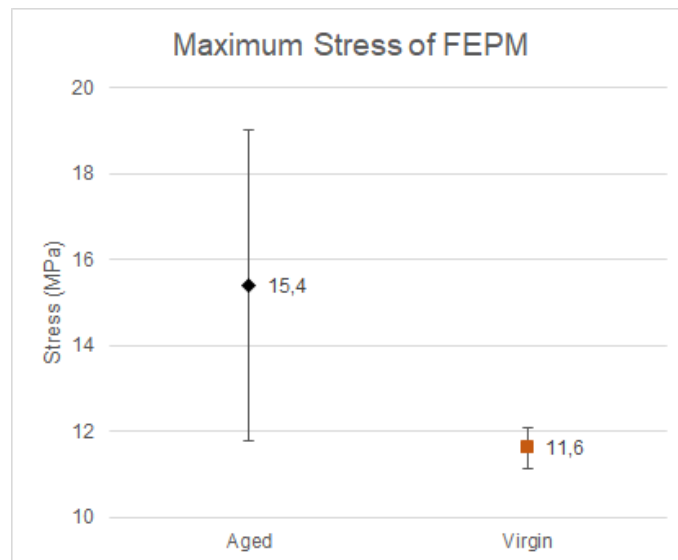
Figure 34 – Compression Stress Relaxation curves of FEPM unaged and 8 week aged in Xylene

Figure 30 a, b and c show the F_0 , namely the maximum stress achieved in CSR tests, of FEPM unaged, aged and a comparison of the average of both conditions, respectively



(a)

(b)



(c)

Figure 35 - Maximum stress of HNBR (a) unaged, (b) aged and (c) average of both conditions

4.5 FKM

4.5.1 Immersion tests

The results of FKM immersed in all fluids for 8 weeks are presented in Figure 36.

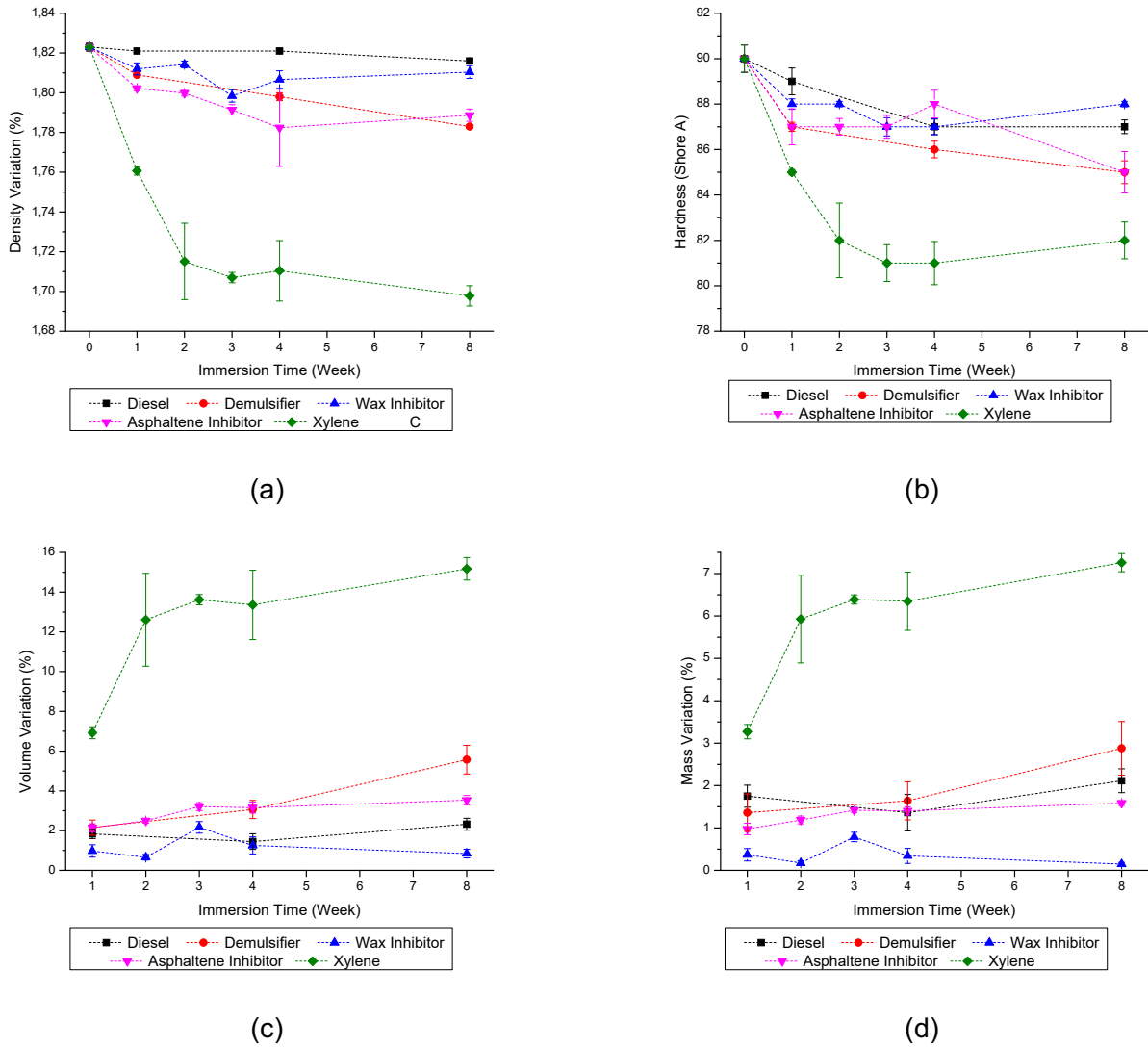


Figure 36 - (a) Density, (b) Hardness, (c) Hardness, (d) Volume and (e) Mass variation of FKM immersed in all six fluids for 4 weeks.

4.5.2 Post-immersion tests

Table 11 presents a comparison data of the results after immersion and after evaporation of mass, volume, density and hardness of FKM immersed in Xylene for 8 weeks. "N/A" stands for "not applicable"

Table 11 - Post-immersion results of FKM immersed in Xylene for 8 weeks

FKM in Xylene (8 weeks immersion)

	Initial	After immersion	After evaporation
Mass variation (%)	N/A	7.3 ± 0.2	$- 1.27 \pm 0.20$
Volume variation (%)	N/A	15.7 ± 0.6	$- 2.20 \pm 0.40$
Density	1.823	1.698 ± 0.005	1.807 ± 0.004
Hardness (Shore A)	90	82	86

4.5.3 FTIR

Figure 37 a to f shows the FTIR spectra of FKM immersed in Xylene.

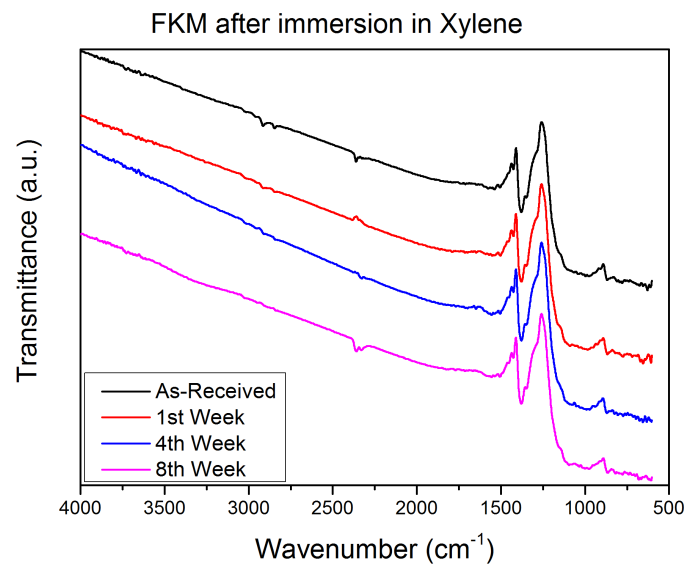


Figure 37 - FTIR curves of FKM in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene

4.5.4 Compression Stress Relaxation

Figure 32 shows the compression stress relaxation curves of FKM unaged and aged in Xylene for eight weeks.

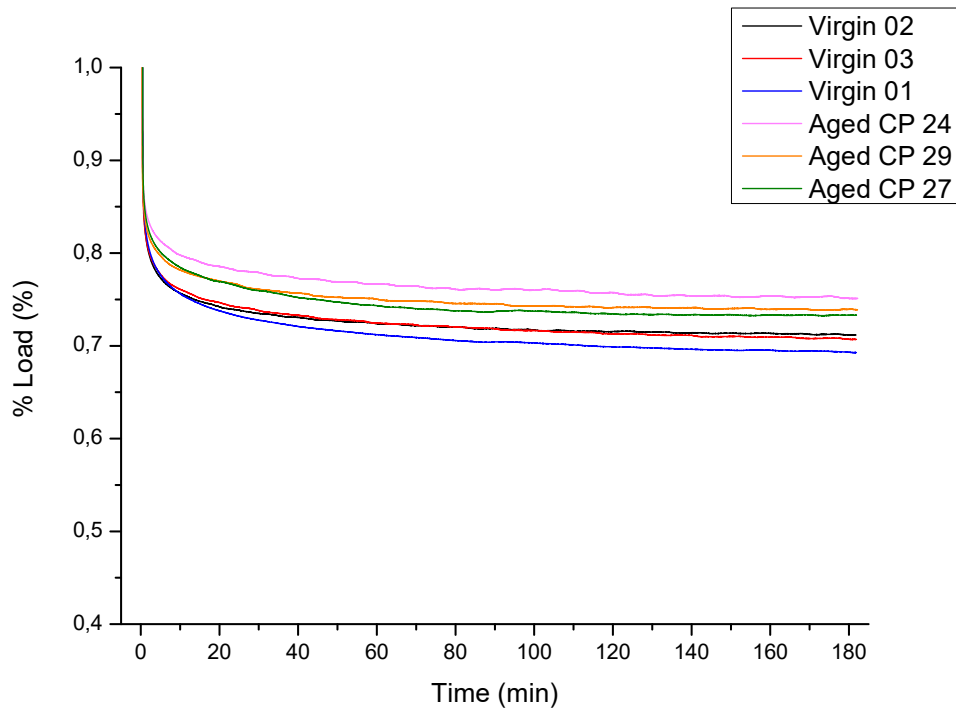


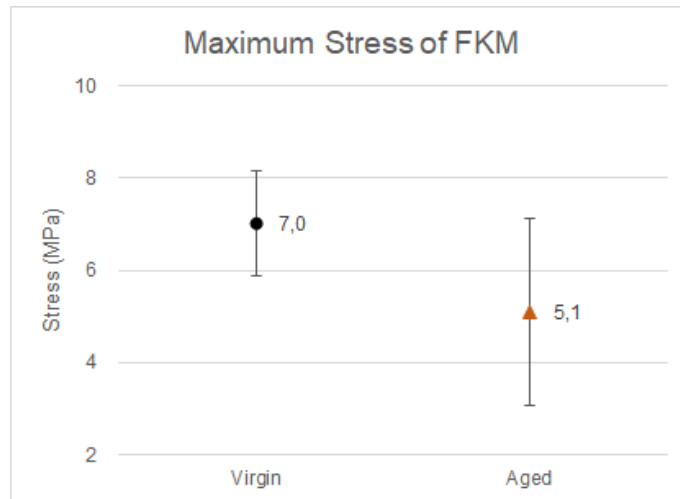
Figure 38 – CSR curves of unaged and aged FKM

Figure 39 a, b and c shows the F0 achieved by FKM unaged, aged and an average of both conditions results respectively.



(a)

(b)



(c)

Figure 39 – F0 of FKM (a) unaged, (b) aged and (c) average of both conditions

4.6 FFKM

4.6.1 Immersion tests

The results of the immersion tests regarding density are presented in Figure 40. Figure 41 a and b presents the results of hardness. In this case, the curves were not presented together due to superposition of some points. The mass and volume variation presented different trends for each fluid, and all data is presented together in Figure 42.

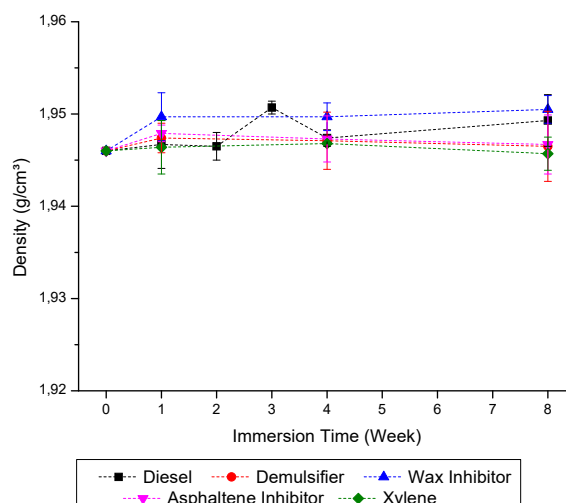
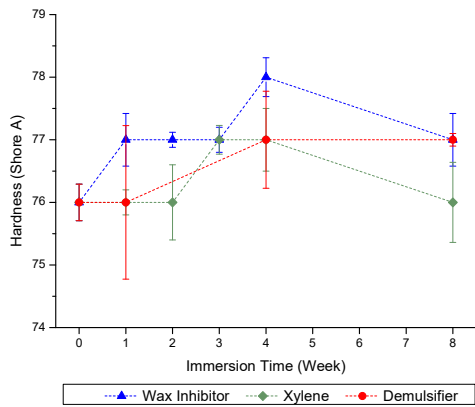
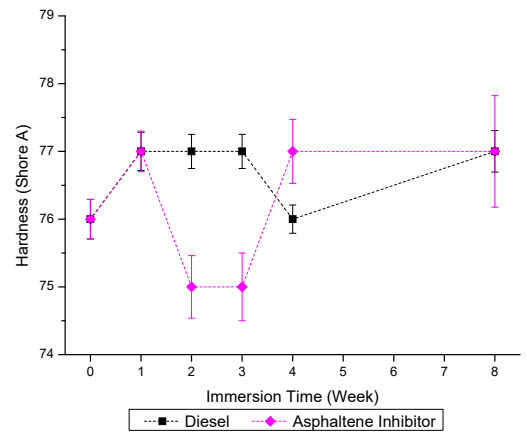


Figure 40 – Density variation along the 8 weeks of immersion of FFKM in (a) Diesel, Demulsifier and Asphaltene Inhibitor, (c) Wax Inhibitor, Xylene and 6th fluid

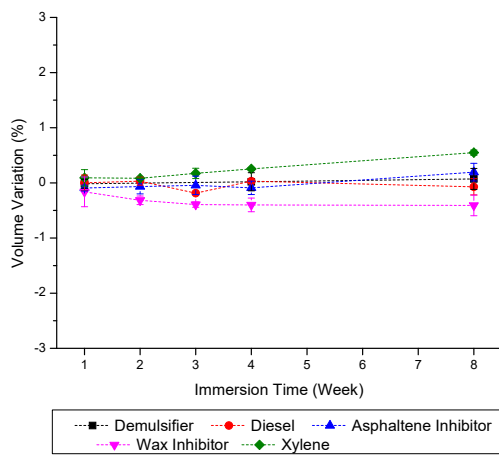


(a)

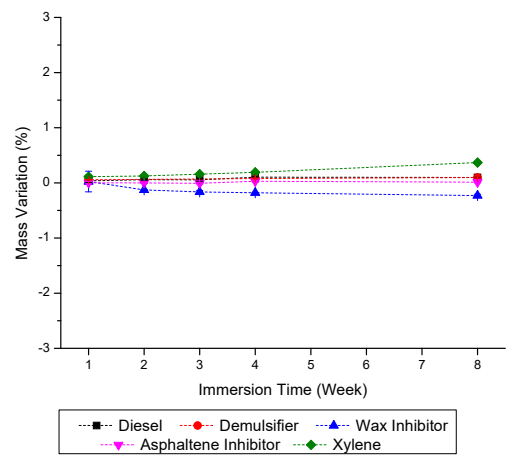


(b)

Figure 41 - Hardness variation along the 8 weeks of immersion of FFKM in (a) Wax Inhibitor, Xylene and Demulsifier and (b) Diesel and Asphaltene Inhibitor



(a)



(b)

Figure 42 – (a) Mass and (b) Volume variation of FFKM along the 8-week immersion in all fluids

4.6.2 Post-immersion tests

The post-immersion results of FFKM immersed in Xylene for 8 weeks are presented below on Table 12. “N/A” stands for “not applicable”.

Table 12 – Post-immersion results of FFKM

FFKM in Xylene (8 weeks of immersion)

	Initial *	After immersion	After evaporation
Mass variation (%)	N/A	0.37 ± 0.02	0.27 ± 0.02
Volume variation (%)	N/A	0.55 ± 0.05	0.39 ± 0.04
Density	1.946	1.943 ± 0.001	1.994 ± 0.003
Hardness (Shore A)	76	76	76

4.6.3 FTIR

Figure 43 shows the FTIR spectra of unaged and aged samples in Xylene.

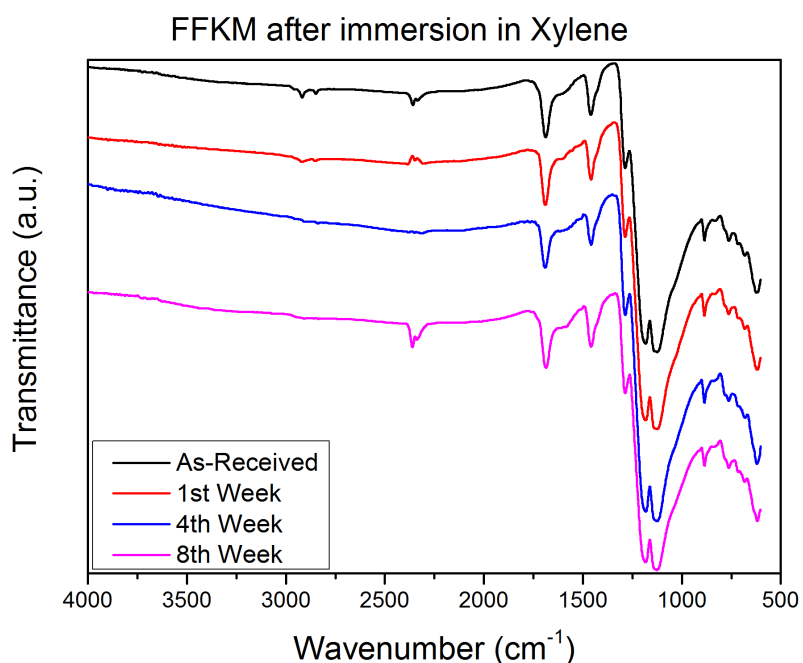


Figure 43 - FTIR curves of FFKM in the conditions unaged and aged after 1, 4 and 8 weeks in Xylene

5 Discussion

5.1 Nitrile Rubbers

All immersion tests resulted in an increase in mass and volume and decrease in density and hardness. These results are not unexpected, since the swelling reduces the polymer chain entanglement [29], leading to a decrease in hardness. Table 13 shows an overview of the comparative results of the immersion tests. It was used a numerical scale from 1 to 4, being 1 the lowest variation and 4, the highest. It is important to highlight that for NBR and HNBR the same trend was observed in each immersion fluid, so the results presented below are valid for both of them. Moreover, since the results of NBR and HNBR were very similar, there is a possibility that the NBR grade used presents high content of ACN. This would lead to lower level of unsaturation and, then, justify the performance similar to HNBR (that possess low level of unsaturation due to hydrogenation of butadiene units) [9] .

Table 13 – Comparative results of 8-week immersion tests of nitrile rubbers

	<i>Mass</i>	<i>Volume</i>	<i>Density</i>	<i>Hardness</i>
<i>Diesel S-10</i>	2	2	2	2
<i>Demulsifier</i>	2	2	2	2
<i>Wax Inhibitor</i>	1	1	1	1
<i>Asphaltene Inhibitor</i>	3	3	3	3
<i>Xylene</i>	4	4	4	4

Xylene was the most aggressive fluid for the nitrile rubbers. As mentioned in 2.1.1, these rubbers do not present good resistance to swelling when immersed in aromatic hydrocarbons. When immersing NBR and HNBR in Xylene for 8 weeks, similar results were found. A final mass increase of 43% and 45%, for the former and the latter, respectively, and a hardness decrease from 90 Shore A to 71 Shore A (-21%) were observed.

Regarding the post-immersion tests, performed with the samples immersed in Xylene, both materials' hardness after evaporation returned to the original value (unaged

condition). Also, both elastomers present a mass and volume decrease comparing to its unaged mass. HNBR presented a higher decrease in volume than in mass, which could be due to crosslink and chain scission, leading to a denser network structure [30].

As shown in 4.1.1 and 4.2.1, Xylene became orange and yellow colored when NBR and HNBR were immersed in it, which is an indicative that some constituent was extracted from the rubbers and migrated to the fluid. As mentioned in 2.1.1, sulfur is a usual agent of vulcanization and sulfates may be used as additives, and its natural form is yellow-colored [31]. There is a chance that some sulfur was extracted, dyeing the fluid. Weitao *et. al.* [30] says that “due to swelling effect, the oil diffused in to the samples and extracted the smaller molecules and additives”, which could be the same mechanism occurring in the NBR and HNBR’s immersion test in Xylene. The FTIR results show that there are no differences in the surface’s chain structure after the immersion test, which is consistent with the theory that only additives were extracted.

When HNBR was submitted to Compression Stress Relaxation, it was observed that the aged and the unaged samples presented similar curves, even with some possible extraction of additives after the immersion in Xylene. However, the aged samples were stiffer than the unageds, achieving higher F_0 , which is the maximum stress. The aged samples reached average stress values 118% higher than the average reached by unageds. As mentioned by Chuango *et. al* [32], the nitrile (CN) can act as active sites to initiate crosslink, and the degradation of HNBR and NBR generally occurs by chain scission and crosslinking. This crosslinking lead to a tighter network structure [33], [30] and could explain the increase in stiffness observed in the aged samples after evaporation. The probable loss of plasticizer suggested by the post-immersion tests results could also explain this increase in stiffness.

NBR and HNBR immersed in Asphaltene inhibitor (AI) presented a higher mass and volume increase at the first and second week, and after this period these values started to decrease (comparing to the former data). NBR values for density and hardness have similar behavior, as seen in most cases. However, for HNBR the second- and third-week measurements shows an opposite behavior. Density increases slightly, but hardness shows a steep decrease. Moreover, on the 4th and 8th week the hardness and density follow the same trend of variation, decreasing density and also decreasing hardness. Although this behavior differs from the observed for other rubbers and other fluids, it is not reasonable to assume that this is an experimental error since the standard deviations observed are small and may not be statistically representative. Yi-Hua *et al.* [34] observed a similar behavior of hardness variation when immersing NBR in a transformer

oil. Even though the chemical composition of AI is unknown, this is one more indication that the results found in the test performed are valid.

When immersed in Demulsifier, NBR and HNBR presented similar results regarding mass, volume, density and hardness. With exception of hardness values, 80 Shore A for NBR and 82 Shore A for HNBR, all other data might be assumed as even, due to standard deviation.

Considering the effects of Asphaltene Inhibitor and Demulsifier on the nitrile rubbers and the poor resistance to polar fluids, there's a possibility that some or both of them are polar. However, the swelling of nitrile rubbers exposed to Demulsifier was not so expressive (6%) and it is difficult to classify exactly if the materials are resistant or not to the fluid. If the NBR used in this presents indeed high level of ACN, as suggested above, its resistance to polar fluids would be reduced [7]. So, if Demulsifier were actually polar, probably the effects would be higher.

Also, even though nitrile rubbers are expected to resist to alkalis [10], they may suffer hydrolysis when in contact with it [35], leading to degradation of the material and there's also a possible mechanism occurring. Other possible mechanisms of degradation are extraction of additives, diminution of compatibility of matrix and fillers due to swelling and oxidation [30]. Considering the effects of Asphaltene inhibitor, that exhibits considerable volume variation, this fluid may also be polar or acid since the nitrile rubbers are not resistant to those scenarios.

It is possible to observe that, among all fluids tested, the Wax Inhibitor (WI) was the least aggressive for the nitrile rubbers, leading to a decrease of 2 Shore A in hardness for both materials. The final values of hardness remain inside the range of regular and acceptable deviation of ± 5 Shore A, given by the supplier and presented in Table 4. Considering that the nitrile rubbers are resistant to non-polar fluids [7] and that the immersion on WI lead to negligible swelling, there's a possibility that this fluid is non-polar and, then, did not degrades the rubber.

HNBR and NBR presented similar results when immersed in Diesel. The major differences are that NBR presented lower hardness at the end of the test, while HNBR presented higher volume increase. Moreover, HNBR clearly did not reach stabilization within the period of 8 weeks, while NBR shows at least a tendency of stabilization. The hardness values present a marked change over the test period, achieving a final value of 80 Shore A for NBR and 83 Shore A for HNBR. It is not possible to clearly determine if the rubbers reached stabilization of mass and volume variation due to great dispersal and to lack of data from intermediate periods. Nitrile rubbers are known to present good

resistance to fuels, and the swelling could be due to relaxation of polymer chains and absorption of the fluid [11]

Although the literature mentions the resistance of the elastomers to some fluids, it is not well defined the parameters used to determine if is compatible or not, like acceptable degree of swelling or hardness variation. Additionally, the acceptable variation of properties is directly related to the application and usually the mechanical properties shall also be evaluated to determine the compatibility. Pickett and Lemcoe [36] say that “a rule of thumb sometimes used to evaluate such data is: volume change less than 16%, elastomer-liquid probably compatible; volume change less than 40%, elastomer-liquid may be compatible; volume change greater than 40%, elastomer-liquid incompatible”. Using these parameters, below on Table 14 is presented a summarized compatibility information. Pruett [37] presents a description of attack based on the volume swelling and loss of tensile strength, and the correlation of the results presented in this study and this classification, based only on the volumetric swelling, are presented in Table 18.

Table 14 – Summarized compatibility between nitrile rubbers and test fluids

	<i>NBR</i>	<i>HNBR</i>
<i>Diesel S-10</i>	Probably compatible	Probably compatible
<i>Demulsifier</i>	Probably compatible	Probably compatible
<i>Wax Inhibitor</i>	Probably compatible	Probably compatible
<i>Asphaltene Inhibitor</i>	May be compatible	May be compatible
<i>Xylene</i>	Incompatible	Incompatible

Table 15 - Correlation between the fluids and the classification presented by [37]

Symbolic Rating	Volumetric Swelling	Description of attack	Fluids
A	≤ 15% in 30 days to 1 year	Excellent, little or no swelling	Diesel, Demulsifier, Wax Inhibitor
B	≤ 30% in 30 days to 1 year	Good chemical resistance. Minor chemical attack, swelling	Asphaltene Inhibitor
C	≤ 50% in 30 days to 1 year	Limited chemical resistance. Moderate chemical attack. Conditional service	Xylene
NR	≥ 50% immediately to 1 year	Severe attack, swelling. Not recommended	

5.2 Ethylene-propylene Diene Rubber (EPDM)

EPDM was the most affected rubber by most fluids among the elastomers tested, presenting a considerable mass, volume and hardness variation already in the first week of test. Table 16 presents the comparative results of the immersion tests after 8 weeks using a numerical scale, where 1 stands for the lowest variation and 4, the highest.

Table 16 - Comparative results of 8-week immersion tests EPDM

	Mass	Volume	Density	Hardness
Diesel S-10	4	4	4	2
Demulsifier	1	1	1	1
Wax Inhibitor	1	1	1	1
Asphaltene Inhibitor	2	2	2	2
Xylene	3	3	3	2

The immersion in Diesel lead to final mass and volume variation of 90 and 119% respectively. Similar results regarding mass variation were found by Haseeb et al. [11] when immersing an EPDM in Diesel, and the swelling phenomena was attributed to the absorption of the fluid and the relaxation of the elastomer's chains. This enormous volume variation is not unexpected, since EPDM shows poor resistance to aromatic hydrocarbons [38].

The immersion on Xylene, also an aromatic hydrocarbon known to affect EPDM, resulted similarly in great variations in mass, volume and hardness (+ 75.5, +78.8 and -18% respectively). It is important to note that in the second week of immersion the rubber's density achieved values close to the water's due to the higher increase in volume than in mass.

Regarding the hardness results of EPDM immersed in Xylene, a steep decrease is observed right in the first week, followed by an increase in the second week and nearly stabilization. Analogous results were observed by Haseeb et al. [11] but no reason was attributed to it is the study.

The FTIR analysis did not show any differences between the aged and unaged samples. As suggested by [39], the ageing of EPDM occurs by chain scission in the propylene segments, which would lead to differences in the spectra, and crosslinking. Also, additional crosslink via termonomer could have occurred during immersion. [39]. To validate this assumption, it would be necessary to evaluate the crosslink density, since no variations were observed on the FTIR spectra of the aged samples

Xylene may have cause an acid induce hydrolysis of crosslink [40] during immersion. It is somewhat expected that the hydrolysis would lead to a decrease in stiffness [9] and, then, to a lower F_0 , the maximum stress, in the Compression Stress Relaxation tests. However, the aged samples presented an F_0 60% higher than the unaged samples.

Susanta et al. [40] reported an analogous behavior when tensile testing aged EPDM, and suggests that there is an optimum degree of crosslink that increases the tensile strength. It was observed that the increase in crosslink lead to an increase in tensile strength until an optimum level of crosslink. After this point is reached, the tensile strength starts to decay even with increasing crosslink density. The authors also suggest that the hydrolysis may have altered this optimum level and could explain the first steep decrease and further increase in tensile strength observed in their study. The same mechanism could have happened and would explain the increase in stiffness.

The post-immersion test suggests that some component was extracted during immersion, but this extraction altered (after evaporation) only its mass and volume, not

the hardness, in comparison to the unaged data. The additives, plasticizers or fillers that were possibly extracted could also lead to an increase in stiffness during the CSR tests.

The immersion in Demulsifier and in Wax Inhibitor presented similar results and lead to only small variation on mass (3.2 and 2.1%), volume (4.7 and 3.7%) and hardness (from 87 to 84 and 85, within the ± 5 Shore A range provided by supplier). As mentioned in 2.1, EPDM presents good resistance to alkalis and polar fluids, while nitrile rubber presents poor resistance to polar fluids. Considering that the Demulsifier was more aggressive to nitrile rubbers than to EPDM, there is a chance that this fluid is polar. Although this chapter concerns EPDM, it is important to highlight that this suggestion is only acceptable if the nitrile rubbers present a high level of acrylonitrile content that would increase its polarity and, then, the assumption would be consistent to the results found for both EPDM and nitrile rubbers. Furthermore, WI may be alkaline since it did not affect EPDM nor nitrile rubbers, both classes resistant to alkalis.

The immersion on Asphaltene Inhibitor (AI) also lead to great swelling, resulting in an increase of 43% in mass and 54% in volume. Considering that EPDM has poor resistance to non-polar and acid fluids, there is a possibility that AI presents some of these characteristics and, then, severely affected the material. Moreover, nitrile rubbers (which suffered considerable swelling when immersed in AI) are more affected by acids than by alkalis, and are resistant to non-polar fluids. So, if Asphaltene inhibitor were non-polar, it would not be consistent to the results observed for nitrile rubbers. Consequently, it is more probable that AI acid.

Still regarding Asphaltene Inhibitor, the 2nd week of immersion results of hardness contrasts. In this point, the hardness achieves the lowest value among all data, reaching 59 Shore A. Since the hardness measurements are made in triplicate and the results is the average of those measurements, the possibility of these points being an outlier are small.

As above-cited, similar results were reported by Haseeb et al. [11] and Susanta et al. [40] when ageing EPDM. The former attributes this results to acid induced crosslink hydrolysis. If AI has an acidic characteristic, similar mechanism of hydrolysis could have happened and would explain the increase in stiffness after the first steep decay.

The same parameters suggested by Pickett [36] and Pruett [37] and used for nitrile rubbers to define compatibility of the elastomer and the fluids are used herein and presented in Table 17 and Table 18. "Probably compatible" is used when volume variation is lower than 16%, "may be compatible" for volume variation between 16 and 40% and "incompatible" for variation higher than 40%. It is important to highlight that,

due to the results obtained in this work, Table 18 only correlates the volumetric swelling and the effects, even though Pruett [37] also uses tensile strength variation to define the effects.

Table 17 - Summarized compatibility between EPDM and test fluids

<i>EPDM</i>	
<i>Diesel S-10</i>	Incompatible
<i>Demulsifier</i>	Probably compatible
<i>Wax Inhibitor</i>	Probably compatible
<i>Asphaltene Inhibitor</i>	Incompatible
<i>Xylene</i>	Incompatible

Table 18 – Correlation between the fluids and the classification presented by [37]

Symbolic Rating	Volumetric Swelling	Description of attack	Fluids
A	≤ 15% in 30 days to 1 year	Excellent, little or no swelling	Wax Inhibitor, Demulsifier
B	≤ 30% in 30 days to 1 year	Good chemical resistance. Minor chemical attack, swelling	
C	≤ 50% in 30 days to 1 year	Limited chemical resistance. Moderate chemical attack. Conditional service	
NR	≥ 50% immediately to 1 year	Severe attack, swelling. Not recommended	Asphaltene Inhibitor, Xylene, Diesel

5.3 Fluorinated rubbers

FFKM was the least affected rubber regarding the mass, volume and hardness variation. Xylene was the most aggressive fluid for this material, leading to a mass variation of 0.37%, volume variation of 0.55% and resulted in a final hardness of 76 Shore A. However, even in this worst scenario, the variations are almost negligible. Although it may seem that the density and hardness varies greatly along the test due to the graph scale, the variation is negligible for all fluids. The highest variation observed in density was of + 0.2% for immersion in Wax Inhibitor. Regarding hardness, an increase of 1.3% (from 76 to 77 Shore A) was observed in the samples immersed in Diesel, Demulsifier, Asphaltene Inhibitor, Wax Inhibitor and Xylene. Considering the standard deviation and the inherent errors to the measurements, already exposed in this chapter, the FFKM can be considered to have reached the stabilization in all the fluids tested.

Considering this scenario, the discussion presented herein will be focused mainly on FEPM and FKM. Table 19 and Table 20 below show an overview of the comparative results of the immersion tests of FEPM and FKM respectively. A numerical scale from 1 (the lowest) to 5 (the highest) is used to show the variation.

Table 19 – FEPM comparative data of 8-week immersion tests

	<i>Mass</i>	<i>Volume</i>	<i>Density</i>	<i>Hardness</i>
<i>Diesel S-10</i>	2	3	3	3
<i>Demulsifier</i>	1	2	2	2
<i>Wax Inhibitor</i>	1	1	1	1
<i>Asphaltene Inhibitor</i>	3	4	4	4
<i>Xylene</i>	4	5	5	5

Table 20 - FKM comparative data of 8-week immersion tests

	<i>Mass</i>	<i>Volume</i>	<i>Density</i>	<i>Hardness</i>
<i>Diesel S-10</i>	2	3	1	2
<i>Demulsifier</i>	4	4	3	3
<i>Wax Inhibitor</i>	1	1	2	1
<i>Asphaltene Inhibitor</i>	3	2	3	3
<i>Xylene</i>	5	5	4	4

Regarding the immersion in Diesel, FEPM presented a variation of 5.3 and % in mass, 9.1% in volume and -4% in hardness (from 93 to 89 Shore A, within the acceptable range from datasheet). However, the rubber did not reach stabilization within this period. None of the rubbers were severely damaged by this fluid. The most affected rubber by Diesel was the FKM, suffering a decay of 2% in hardness. Moreover, the results of volume variation of FFKM immersed in Diesel present an erratic behavior, showing an oscillation between volume increase and volume decrease in the subsequent retrieval. This may be either a characteristic of the material of plasticizer loss [41] or an inherent error of the measurements since the variations are all close to zero.

The immersion in Asphaltene Inhibitor (AI) was more aggressive to FEPM than to FKM, leading to a mass variation of 9 and 1.6% respectively. The fluid lead to an increase in volume of 16 and 3% for each rubber. FFKM swelling was negligible. FEPM is expected to have lower resistance to acids than FKM and FFKM [21], so there is a possibility that AI is acid since this rubber was more affected by AI than FKM and FFKM. If AI is actually acid, it would also justify the low effect on FKM and FFKM, the comparative higher effect on FEPM and the swelling degree of the nitrile rubber and EPDM, as presented in 5.2 and 5.3.

Regarding the immersion in Wax Inhibitor, FFKM and FEPM presented a mass decrease while FKM, mass increase. The Wax Inhibitor may have dissolved the soluble additives of FEPM and FFKM and extracted them [30] or could have led to plasticizer loss [41], leading to a final mass decrease. Both rubbers have TFE as one of the monomers of the main chain, so maybe this monomer is somewhat affected by Wax Inhibitor. While FEPM

presented a volume increase of 0.25%, FFKM presented a volume decrease of 0.41%. However, those variations did not alter significantly the hardness, which may be due to a counterbalance of fluid absorption and loss of plasticizer. The FFKM presented the smallest variation in density and a negligible hardness increase, but led to the higher, although also very small, mass variation. The immersion in WI led to an increase in mass and volume of FKM and a decrease in density and hardness. Overall, FKM was most affected than FEPM and FFKM, albeit the variation was still negligible.

The immersion in Demulsifier led to greater swelling and hardness decrease of FKM than of FEPM. Moreover, this fluid was one of the least aggressive to the fluorinated rubbers, leading to a general variation higher than on Wax Inhibitor. As mentioned in 2.1.3, FEPM presents better resistance to alkalis than FKM, which is in agreement with the results observed herein. The results observed for the other rubbers, discussed in 5.1 and 5.2, suggest that Demulsifier may be alkaline, which is compatible with the results for fluorinated rubbers.

Xylene was the most aggressive fluid for all fluorinated rubbers, and FEPM was the most affected among them. A final reduction of 13% in hardness (from 93 to 81 Shore A), an increase of 19% in mass and 34% in volume were observed. The curves are basically linear and constant from the beginning, presenting a clear trend of stabilization just after the second retrieval.

Regarding FFKM immersion in Xylene, it is possible to observe that the hardness was not modified. Moreover, Xylene led to the higher mass and volume increase observed for this rubber. It is important to highlight that the highest variation, in modulus, was observed for immersion in Wax Inhibitor.

The FTIR data suggests that Xylene led to some modifications on the elastomers' structure (chain, bonds and/or additives) since a progressive reduction of the peaks associated to CH_2 and CH_3 ($2980 - 2850 \text{ cm}^{-1}$) was observed for all fluorinated rubbers. This decrease was also observed by Kader & Bhowmick [42] and was associated to the "removal of ethyl group from ester unit leaving behind only methine groups on the backbone". Moreover, the 1290 and 790 cm^{-1} peaks also presented a decrease in intensity in the FEPM spectra, which means that the rubber structure was affected by the fluid. This is in accordance with the post-immersion test that shows a slight decrease in mass of FEPM after evaporation of Xylene.

Regarding FKM, when its mass and volume were measured after evaporation of Xylene, it presented a decrease of 1.2% in mass and 2.2% in volume, relative to the original mass (pre-immersion). It is probable that most of the Xylene evaporated and some of the

rubber's constituent (such as additives and plasticizers) have been extracted during immersion. The FKM presents a different post-immersion behavior related to hardness. It was the only material that did not return to initial hardness (i.e., values measured before the immersion) after the evaporation of Xylene. The immersion lead to a permanent decrease in 4.5% of hardness, reaching 86 Shore A. However, as already mentioned in the previous discussions, the supplier stands that the hardness is 90 ± 5 Shore A, so the value measured falls within this regular range.

The compression stress relaxation tests of FKM shows that the ageing in Xylene altered the compressive behavior of the rubber. While the F_0 achieved of the aged samples were lower than the F_0 of unaged samples, the stress decay of the unageds was more intense. The Xylene may have acted as a plasticizer, reducing the chain entanglement and, consequently, leading to a reduction on rubber's mechanical properties [43].

FEPM presented the opposite behavior when submitted to CSR tests. The aged samples achieved greater F_0 values, while the stress decay curves presented the same trend as unaged's curves. Thus, it is not possible to clearly define the ageing effects based on the CSR curves. Considering that after evaporation mass, volume and hardness of the aged samples returned to original values, it is possible that the immersion in Xylene did not lead to permanent effects of the rubber.

Regarding the post-immersion tests, FEPM mass variation between the as-received condition and after Xylene's evaporation was nearly negligible. Density may be considered unchanged when evaluating the standard deviation. Analyzing the hardness data before and after immersion, it can be understood that the hardness decrease just after immersion was due to the swelling, since the hardness after evaporation returned to the original value. This may indicate that the material present good resistance to Xylene chemical attack. It is usual that some variation in properties occur when the material is directly immersed in some fluid due to swelling.

FFKM was the only material that presented a mass and volume increase in the post-immersion test, comparing to the unaged values. Considering that the swelling was very low, in some way the molecules of the polymer are tightened enough to prevent the fluid to absorb. Since the fluid, apparently, did not alter the chain entanglement (based on the hardness variation [29]), the desorption of the fluid would also be encumbered and justify the mass variation observed in the post-immersion tests.

Table 21 presents a summarized compatibility information based on the classification suggested by [36]. The elastomers are classified as "probably compatible" when volume variation is lower than 16%, "may be compatible" for volume variation between 16 and

40% and “incompatible” for variation higher than 40%. *Table 22* shows the correlation between the immersion fluids and the effects on the materials, based on the criteria presented by Pruett [37]. It is important to highlight that even though Pruett [37] used both volumetric swelling and changes in tensile strength to define the effects, only the volume variation was considered in the table due to limitation of the results.

Table 21 - Summarized compatibility between fluorinated rubbers and test fluids

	<i>FEPM</i>	<i>FKM</i>	<i>FFKM</i>
<i>Diesel S-10</i>	Probably compatible	Probably compatible	Probably compatible
<i>Demulsifier</i>	Probably compatible	Probably compatible	Probably compatible
<i>Wax Inhibitor</i>	Probably compatible	Probably compatible	Probably compatible
<i>Asphaltene Inhibitor</i>	May be compatible	Probably compatible	Probably compatible
<i>Xylene</i>	May be compatible	Probably compatible	Probably compatible

Table 22- Correlation between the fluids and the classification presented by [37]

Symbolic Rating	Volumetric Swelling	Description of attack	Fluids
A	≤ 15% in 30 days to 1 year	Excellent, little or no swelling	Diesel, Demulsifier, Asphaltene Inhibitor (FKM), Wax Inhibitor
B	≤ 30% in 30 days to 1 year	Good chemical resistance. Minor chemical attack, swelling	Xylene Asphaltene Inhibitor (FEPM)
C	≤ 50% in 30 days to 1 year	Limited chemical resistance. Moderate chemical attack. Conditional service	
NR	≥ 50% immediately to 1 year	Severe attack, swelling. Not recommended	Asphaltene Inhibitor, Xylene, Diesel

6 Conclusion

Generally, all rubbers presented a mass and volume increase when submitted to immersion tests. The swelling lead to a reduction in chain entanglement [11] [29], and consequently a decrease in hardness. Overall, the EPDM was the most affected elastomer, followed by nitrile rubbers which shown an intermediate performance and fluorinated rubbers which were the least affected. Moreover, FFKM was virtually unaffected by all fluids, and probably the variations observed were not statistically considerable.

Xylene was the most aggressive fluid to the elastomers, with exception of EPDM. Nitrile rubbers and EPDM show poor resistance to aromatic hydrocarbon [7], so it was expected that Xylene would lead to great swelling. Indeed, the highest volume variation observed were of NBR, HNBR and EPDM: 67, 68 and 99% of volume increase respectively. However, the FTIR analysis did not show modifications on the chains of these elastomers after immersion in Xylene.

Furthermore, the fluorinated rubbers observed the lowest volume variation, reaching 19, 7 and 0.4% increase for FEPM, FKM and FFKM respectively. The fluid lead, though, to modifications of the elastomers' structure, since a reduction of the peaks associated to CH_2 and CH_3 ($2980 - 2850 \text{ cm}^{-1}$) was observed. This is probably due to the removal of ethyl group [42]. However, it is important to highlight that even with that degradation, the hardness of the rubbers returned to original value when the fluid evaporated. Since the post-immersion tests suggests that some components were extracted from the rubbers, one possibility is that some plasticizer was lost and it counterbalanced the effects of degradation of the chains.

The Compression Stress Relaxation tests performed with the 8-week aged samples in Xylene resulted in similar curves than the unaged's. Moreover, the maximum stress achieved in the test, namely F_0 , was clearly higher for aged samples of HNBR, EPDM and FEPM. Regarding FKM results, it is not possible to accurately affirm that the opposite is true (lower F_0 for aged samples) due to standard deviation.

FFKM, known to present outstanding chemical resistance [6], was the least affected rubber by all five immersion liquids used in this study. All volume variations were lower than 0.6%. However, it presented different behavior in some cases. When immersed in Wax Inhibitor, the least aggressive fluid for all rubbers, it presented a mass decrease rather than increase. The volume variation was close to the one observed in Xylene's immersion (0.41 and 0.55% respectively). Moreover, FFKM was the only rubber that after evaporation observed a mass increase comparative to the mass before immersion. It

was suggested that since it present great resistance to absorption of fluid and its chains did not suffer high relaxation due to swelling, the evaporation of fluids would also have been encumbered.

The immersion in Diesel was severely aggressive only to EPDM. This elastomer, as above-cited, has poor resistance to aromatic hydrocarbons and the results were not unexpected. The ageing test led to a decrease of 14% in hardness and reduced the density so intensely that it achieved values lower than water's density.

The nitrile rubbers presented very similar results in all immersion tests. HNBR has lower level of unsaturation than NBR due to hydrogenation of butadiene units [9], so it was expected that would present a better performance. Considering that the resistance of nitrile rubbers is improved with increase of acrylonitrile (ACN) content, one possible scenario is that the grade of the NBR used present high levels of ACN. This would lead to lower level of unsaturation and, then, to a better performance.

The effects of Wax Inhibitor (WI), Demulsifier and Asphaltene Inhibitor (AI) could not be predicted since the compositions are unknown. However, after the results some assumptions could be done since the general chemical compatibility of the rubbers are consolidated in the literature.

It was suggested that AI may be acid, since the both nitrile rubbers and EPDM show lower resistance to acidic fluids and were severely affected by Asphaltene Inhibitor. Also, acid fluids would probably affect FEPM more than FKM, since generally FEPM has better resistance to alkalis than FKM [6].

Regarding Demulsifier, if this fluid is an alkali, the results of the test would be in accordance with what should be expected. As above-cited, FEPM is likely to present better resistance to alkali than FKM, and this was observed in the results. Moreover, Demulsifier had little effect on volume variation of EPDM and nitrile rubbers, which are resistant to alkalis.

Wax Inhibitor, although the least aggressive fluid, was the only one that lead to mass decrease in any rubber. While both FEPM and FFKM observed this mass decrease, just FFKM had its volume diminished. It is possible that Wax Inhibitor diffused into the polymer and dissolved some additives or lead to plasticizer loss [30] [41]. This assumption would also explain the negligible hardness variations of these rubbers after immersion in WI. Since the swelling was low in all immersion tests of WI and it is expected that all of the elastomers present good resistance to alkaline medias, there is a possibility that Wax Inhibitor presents alkaline characteristics.

7 References

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