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ANALYSIS OF VARIOUS POLYMER PARTS IN CONTACT WITH BIODIESEL

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Abstract:

In this paper, several parts consisting of polymeric materials are studied, in order to determine if they are affected when they are kept in contact with biodiesel at constant temperature and pressure. The samples used are constituted by polymers of silicone (S), acrylonitrile (AN) and propylene hexafluor (Viton-V7). These materials have been selected for investigation because they form part of an industrial process in which they are used, and have been observed early wear characteristics thereof. They consist of seals and cords which are in contact with biodiesel. These materials were kept immersed in biodiesel at atmospheric pressure at a temperature of 40°C for time periods up to 120 days. Virgins tested ones are characterized by various techniques: OM, SEM, XRD, DTA-TGA, among others. Viton sample was the least affected by treatment, while the acrylonitrile sample is the one that has shown the greatest variations.

Keywords: biodiesel; polymers; wear; silicone; acrylonitrile.

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1. Introduction

The combined cycle power plants use as alternative fuels to coal, other fuels such as natural gas, fuel oil and biodiesel. From the economic point of view, natural gas is the most convenient in Argentina, but its supply is limited in winter. In periods of restriction of natural gas, fuel oil or mixtures of fuel oil and biodiesel replace it.

Biodiesel is a mixture of esters formed by condensation of methanol and different fatty acids. The industrial scale production of biodiesel is performed by a process of transesterification of triglycerides and methanol in the presence of sodium methoxide as alkaline catalyst.

Compatibility studies between biodiesel and elastomers, incorporated into the fuel system in vehicles, have been reported (Rudbahs & Smigins, 2014; Kass et al., 2018). The authors have found that even if volume variations in the pieces that have been in contact with biodiesel are observed, no major changes are detected in the physical properties of these materials.

The influence of palm biodiesel and biodiesel-diesel mixtures on elastomers of nitrile rubber type, polychloroprene and fluorovitons has been investigated by Hasseb et al. (2010), subjecting these materials to immersion at 50°C for 500 hours, observing a significant degradation in the first two hours, while viton showed good resistance to attack. These authors have determined similar results in other experimental conditions, with a greater variety of elastomers such as silicone rubbers, nitrile, polytetrafluoroethylene, polychloroprene, etc., establishing a ranking of degradation for these polymeric materials (Haseeb et al., 2011).

Alves et al. (2013) have evaluated the degradation of elastomers used as o-rings in biodiesel injection systems, analyzing the mechanical properties and deformation of the parts. In this study, biodiesel from palm and biodiesel from soybean, and parts of nitrile and fluorocarbon are used. It is concluded that fluorocarbon samples are the most resistant to degradation in both fuels, and it is found that the nitrile elastomer loses mass in the process due to the high polarity of biodiesel attributed to carboxylic groups present.

The biodiesel that comprises fatty acids saturated and unsaturated alkyl esters, when exposed to air, heat, light and metal contaminants, may cause its autoxidation. This process leads to the formation of corrosive acids and deposits that cause degradation of metals and elastomers.

Bhardwaj et al. (2014) have published an important bibliographical review on the compatibility of metals and elastomers in biodiesel[6] These authors conclude that after having analyzed several metals: copper, brass, aluminum, stainless steel, etc., stainless steel is the one that has suffered the least degradation, and presents the least influence on the properties of biodiesel.

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In this paper the possible affectation of polymeric parts, constituted by nitrile, silicone and viton, that are in contact with biodiesel are analyzed in order to determine the influence of the fuel on the integrity of them when kept in contact at constant temperature and pressure during different time periods.

2. Experimental

The materials used in this study were selected because they are part of an industrial process in which they are in contact with biodiesel, and characteristics of early wear of its parts: seals and ropes seal, have been observed. These parts are constructed with silicone, acrylonitrile and viton elastomers, and will be hereinafter referred to as samples S, AN and V7, respectively. These parts have the same composition that will be used by the manufacturer for the design of the parts that will be adapted to the biodiesel pipes inside the thermal plant. The number of samples was three in each test condition, and the values of the figures are average of those experiences.

In Figure 1 these studied polymeric parts and the samples used for testing, are observed. The parts S and AN have a steel core.

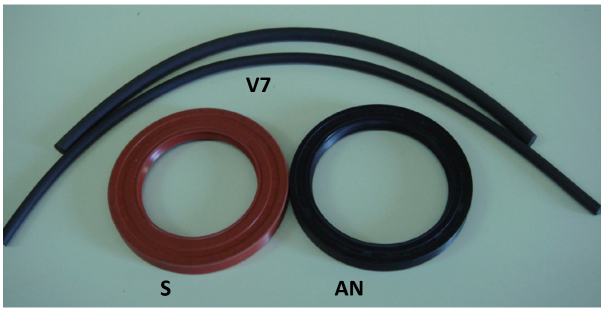

Figure 1: Studied polymeric pieces.

The thermal power plant that uses this materials in its industrial process has provided both the samples and the biodiesel used in this research. The biodiesel used by this company has export quality, this means that it must comply with the IRAM 6515-1 standard, which has been taken into account when developing these studies as a reference for the analysis of biodiesel after contact with the samples.

The development of the tests was conducted by immersing the samples in biodiesel during different periods of time: 15, 30, 45, 60 and 120 days. They were kept in an oven at 40°C, at atmospheric pressure, isolated from light and currents of air.

After each period of time, samples are extracted, dried superficially with a cloth, weighed, and subjected to further drying in an oven at 40°C. During this process, the weight of the samples is periodically checked according to the elapsed time until constant weight.

The starting materials and the recovered after testing 120 days immersion, taken as the probably most affected, have been characterized by diverse techniques: optical microscopy (OM) and scanning electron microscopy (SEM), dispersive X-ray analysis (EDS), and thermogravimetric differential thermal analysis (DTA-TGA), X-ray diffraction (XRD) and surface roughness.

Optical observations were made with a Zeiss-Axiotech equipment with a 3CCD Donpisha camera.

SEM analyzes were carried out with a scanning electron microscope Philips 515, with energy dispersive analyzer EDAX-Phoenix.

The diffraction patterns of X-rays were obtained with PANalytical X'Pert PRO equipment, radiation CuKα (λ = 1.5406 nm). The operating conditions were 40 kV, 40 mA.

DTA-TGA were performed on a Shimadzu DTA-50 TGA-50 equipment with TA-50 WSI analyzer.

The surface roughness of the samples was determined with a equipment DIGIMES Mod. RUG 04 (precision 0.001 μm).

On the other hand, the biodiesel has been analyzed in its virgin state and after 120 days in contact with the polymer parts, by developing standardized tests that lead to determine the contents of total esters and alkyd esters of linolenic acid (EN 14103 standard), determination of iodine value (EN 14111 standard), acid number (IRAM 6558 standard), and oxidation stability (EN 14112 standard).

3. Results and discussion

Semiquantitative chemical analysis by EDS of the samples is presented in Table 1, where the elementary compositions can be seen. The sample called S consisting of silicone polymer, shows in addition to the constituent elements of the monomer (-[O-Si-$(CH_3)_2$]-), small amounts of Ni and Mg.

The constituent elements of acrylonitrile monomer are C, H and N. In Table 1, the presence of small proportions of Si and Zn for this sample is observed, probably in the form of oxides, and sulfur (S), commonly used to increase the mechanical strength of these materials.

V7 has in the composition various monomers consisting of C, H and F, with the presence of unsaturated bonds. For V7 sample, besides C, a significant content of F and also small amounts of Mg, Si and Ca can be observed.

Table 1: EDS analysis of samples

Element [% m/m]	S	AN	V7
C	6.06	86.75	43.30
O	15.60	4.40	5.90
Ni	3.43	---	---
Mg	5.21	---	2.28
Si	69.7	2.77	1.30
F	---	---	38.55
Ca	---	---	2.93
S	---	2.02	---
Zn	---	4.06	---

X-ray patterns of virgin samples show a ridge centered at approximately 2Ə = 16^0, typical indicator of amorphous polymeric materials. In the sample S, the corresponding peaks to cristobalite are observed (SiO_2: pdf 82-1410), probably incorporated as a filler in these materials. The diffraction pattern of the AN sample shows peaks corresponding to zinc oxide (ZnO: pdf 80-0075), and small peaks corresponding to cristobalite. V7 sample pattern presents a large number of peaks that have been identified as polycarbon fluoride ($(C\text{-}F)_n$: pdf 27-1873) and carbon fluoride (C4F: pdf 26-0344). This would indicate the presence of crystalline portions of the base polymer in the studied parts.

Figure 2 shows the weight increase records of samples in relation with the period of time immersed in biodiesel. As it can be seen, the V7 piece has the lowest and practically constant values. Sample AN shows a continuous increase in weight over time immersion, while the S sample presents a strange behavior because until 45 days it maintains its weight of around 5% increase, and then after 60 days it doubles this value, and then return to 5%. This behavior is verified in different experiences carried out.

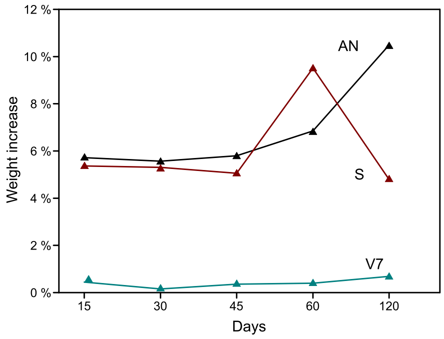

Figure 2: Weight increase of samples *vs*. period of time immersed in biodiesel.

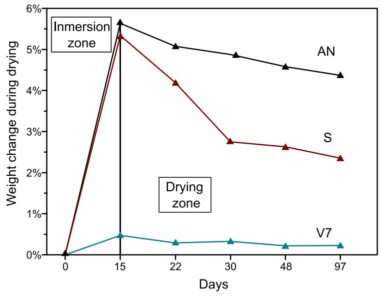

Figure 3: Weight change during drying. Immersion time: 15 days.

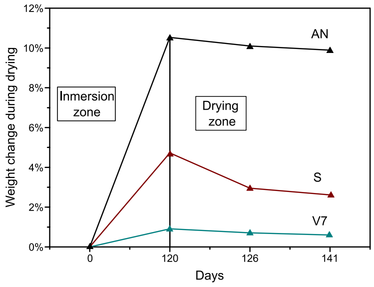

Figure 4: Weight change during drying. Immersion time: 120 days.

The same technique has been used on samples that have been immersed 120 days in biodiesel and the results show that in the case of the sample S the same pattern is obtained, that is, the presence of cristobalite. In AN sample a marked decrease in the presence of ZnO is noted, and in V7 polycarbon fluoride peaks remain assigned, although less intense, and the peaks of the phase C4F disappear.

Figures 3 and 4 show the drying processes of polymeric pieces after being removed from the immersion in biodiesel and maintained in oven at 40 °C. As noted, although their weight change with drying time, none of the tested pieces recovers their original weight, being permanently affected. It is also possible to determine that the longer contact with biodiesel, the impact on the parts in relation to weight is greater.

The observations of the specimens by OM were performed on all virgin samples and those which have been immersed in biodiesel for 120 days.

Figure 5 shows optical micrographs at different magnifications of the AN sample. AN-B identifies the sample that has remained in contact with biodiesel. At low magnifications a modified surface appearance is observed, AN-B sample is shown with a smoother surface but with larger reliefs. At higher magnifications it is observed that these reliefs are due to areas of different morphology and structure, as if they were segregated phases or precipitated compounds adhered to the surface.

The S sample still at low magnification presents a significant change in the surface morphology when the virgin specimens are compared with specimens immersed in biodiesel (S-B). Figure 6 shows images obtained at x100 magnification, where wear areas as craters can be seen in the sample S-B.

OM analysis of V7 sample shows no perceptible differences between the original specimen and the one that has been in contact with biodiesel.

Similar results were obtained in the SEM observations of virgin samples and after immersion for 120 days. Figure 7 shows the segregated or attached phases on surface as mentioned above for the sample AN. EDS analysis of this area shows the same specified composition in the original AN sample (Table 1).

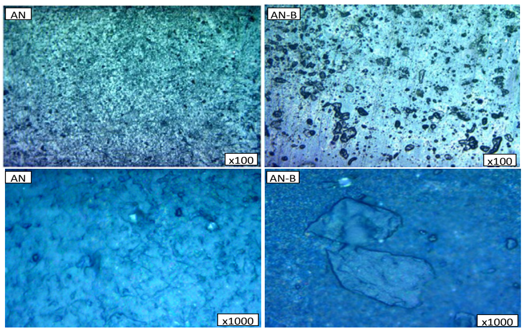

Figure 5: Optical micrographs at different magnifications of AN and AN-B samples.

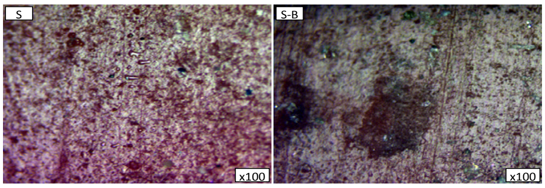

Figure 6: Optical micrographs at different magnifications of S and S-B samples.

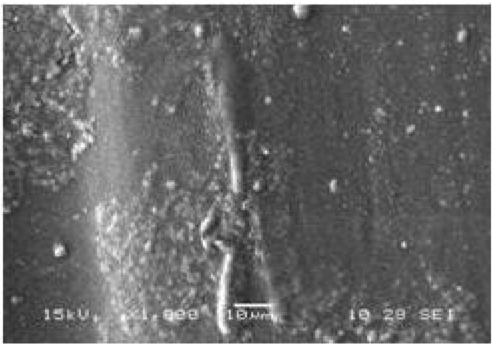

Figure 7: SEM micrographs of AN sample.

The DTA-TGA analysis of virgins and used samples were performed in the range T ambient - 1000°C (Figure 8).

Sample S presents three exothermic peaks in the range 400°C and 700°C, the first one centered at 443°C is a broad peak, and then on it, two other smaller peaks at 541°C and 642°C are presented. Considering that this polymer material is formed by a single monomer, these two small peaks can be interpreted as resulting from the partial combustion products of the former. DTA curve of the used sample S-B, presents similar characteristics, but with the absence of the two small peaks.

As mentioned, V7 sample consists of several different monomers, this is exhibited in a DTA-TGA diagram, with four well defined peaks in the range 400°C-600°C, as shown in Figure 8. The DTA-TGA curve of the V7 sample after the 120 days of contact with biodiesel has an identical appearance to the original sample.

The corresponding results for the AN sample show a very small peak around 415°C, and an area with several intense and sharp exothermic peaks between 480°C and 650°C, both virgin and used materials.

The variation of the surface roughness of the samples is a parameter often used to indicate the alteration of the pieces due to contact with biodiesel. Regarding the samples used in this study it has only been possible to obtain reproducible results in sample S. Figure 9 shows the result of these determinations. It can be seen that all the samples were in contact with biodiesel present lower roughness, even those that have been immersed for 15 days.

As mentioned it was also studied whether biodiesel in contact with polymeric materials has changed its characteristics or properties.

Analyses of the virgin biodiesel and after 120 days are presented in Figures 10 to 13, corresponding respectively to the results of the tests to determine acid number (AN), iodine value (IV), total esters (TE) and alkyl ester of linolenic acid (AELA).

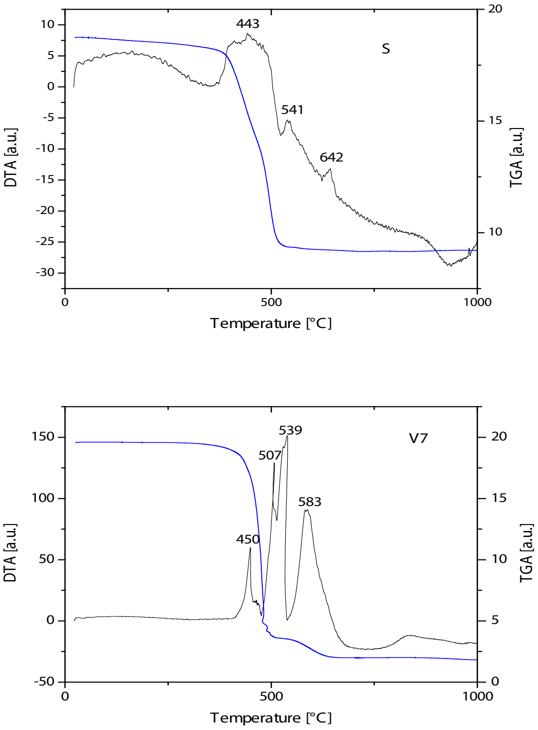

Figure 8: DTA-TGA analysis of the original S and V7 samples.

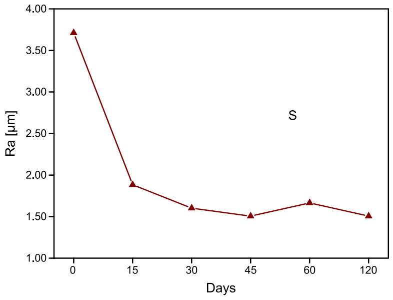

Figure 9: Roughness of the S sample *vs.* immersion time.

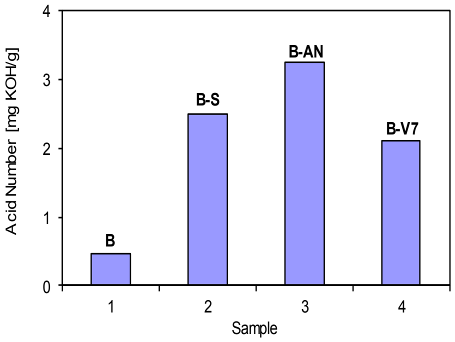

Figure 10: Acid number of the virgin biodiesel (B) and in contact with the S (B-S), AN (B-AN) and V7 (B-V7) samples.

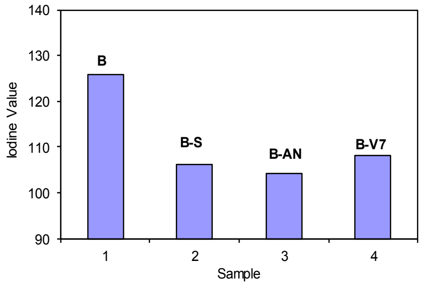

Figure 11: Iodine value of the virgin biodiesel (B) and in contact with the S (B-S), AN (B-AN) and V7 (B-V7) samples.

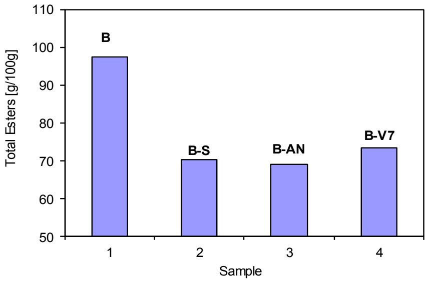

Figure 12: Total esters of the virgin biodiesel (B) and used with the S (B-S), AN (B-AN) and V7 (B-V7) samples

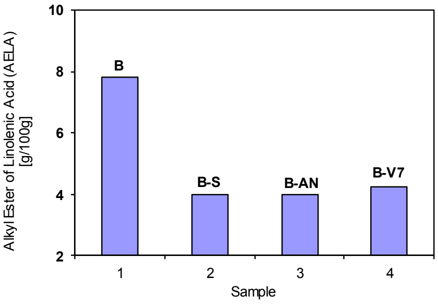

Figure 13: Alkyl Ester of Llinolenic Acid (AELA) of the virgin biodiesel (B) and used with the S (B-S), AN (B-AN) and V7 (B-V7) samples.

As shown in the figures, these parameters determined in the biodiesel are affected in all cases by the presence of the polymeric materials studied, with the largest variation observed for the AN sample and lower for V7 sample.

The oxidation stability at 110°C for virgin biodiesel was 6.3 hours and for all samples of biodiesel used in contact with the polymer specimens was <0.5. Standard specification for this parameter is 6 h (minimum).

All determinations carried out for biodiesel after samples immersion, provide results outside the specifications established by the Standard IRAM 6515-1.

4. Conclusions

In this work various polymeric pieces constituted by nitrile, silicone and viton elastomers in contact with biodiesel were analyzed, in order to determine the influence of the fuel on the integrity of these parts when kept in contact at constant temperature and pressure during different periods of time.

The results of this research enable to conclude that both the tested pieces as well as the biodiesel used, presented affection in its original characteristics and properties permanently after contact.

The sample of acrylonitrile polymer has been the most affected in its characteristics and this specimen has further modified parameters of biodiesel, while the viton polymer sample was the least affected and has produced the fewest variations to the properties of biodiesel.

Acknowledgments

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