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LONG-TERM EFFECT OF DIESEL ON POLYOXYMETHYLENE AT DIFFERENT TEMPERATURES

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Abstract. *Polyoxymethylene (POM) is thermoplastic used to manufacture automotive fuel pump gears and rotors due to its low coefficient of friction and thermal and dimensional stability. In this study, POM was immersed in Diesel at different temperatures (-10ºC, 23ºC and 60ºC) for 1000, 2000, 3000, 5000 and 10000h. After degradation, tensile tests were performed to evaluate the material mechanical properties and analyze the effect of Diesel degradation.*

Keywords: *Polymers, degradation, temperature.*

1. INTRODUCTION

Depending on the function of the selected automotive components, polymers must meet some requirements such as lightweight, chemical resistance, heat resistance, retention of mechanical properties, among other properties and they need to be compatible with the substances in direct contact with them, for example, fuels (Ghassemieh, 2011).

Polymers are materials susceptible to degradation over time. This is a slow and irreversible alteration of its physical and chemical properties. There are two main consequences of aging: physical and chemical.

Chemical aging comes from the reactions between the polymer and the environment. Three different effects can be divided into thermochemical aging, photochemical aging and aging in the presence of reactive agents.

One of the most critical reasons of polymer degradation is oxidation. The union of high temperatures and oxygen presence can lead to a process accelerated oxidation. The formation of hydro-peroxides (POOH) seems crucial in this process, due to they are responsible for one part of the oxidation process (Fayolle, et al., 2008). These reactive induce on the polymer radical chain scission and depolymerization. As a consequence, a mass loss is produced with a progressive embrittlement (Fayolle, et al., 2009). On the other hand, physical aging can come from the free volume relaxation or solvent absorption and migration of additives (David, 2009). When POM is exposed to high temperatures, the polymer chain unzips (depolymerization) into formaldehyde, which then oxidizes into formic acid, this in turn acts as a catalyst and increases the rate that the polymer chain unzips (Wright and Rapra, 2006; Wolford, 1964).

Penetration of the polymer is the first step for aging in presence of diesel, therefore, is the key factor for any quantitative analysis of aging. The interactions due to absorption between the polymer and the diesel have some different aspects, since there is not only one solvent.

From all these sources of degradation, only some of them are present in our case, these are: thermo-oxidation, presence of reactive agents, free volume relaxation, solvent absorption and migration of additives.

Polyoxymethylene (POM) is commonly used as a direct replacement for metals due to its stiffness, dimensional stability and corrosion resistance (Nicholas, 2001). Some examples can be observed in fig. 1.

Figure 1. Examples of polymers substituting metals.

POM has a semi-crystalline structure, where the amorphous phase transmits the forces between the crystalline phases (Celina, 2013). This amorphous phase is also more permeable than the crystalline, hence the oxidation process is performed mainly in this phase. This oxidation leads a chain scission process on the amorphous phase, as well as an embrittlement resulting from the destruction of the entanglement network (Fayolle, et al., 2008). In semi-crystalline structures as POM, this chain scission also produces a secondary crystallization (chemi-crystallization), which increase the crystallinity rate and makes more brittle the polymer (Richaud, et al., 2013) (Fayolle, et al., 2009). This also makes decrease the interlamellar distance between the crystallized parts.

Table 1 shows the mechanical properties of the studied material. The present study aims to determine the effects of diesel on the long-term mechanical properties of POM polymer. To achieve such goal, POM was immersed in Diesel at different temperatures (-10ºC, 23ºC and 60ºC) for 1000, 2000, 3000, 5000 and 10000h. After the degradation period, tensile tests were performed.

Table 1. Mechanical properties of POM.

Parameter	Unit	Value
Yield tension	MPa	70
Alongation	%	25
Young Modulus (tension)	MPa	3000
Young Modulus (bending)	MPa	2620
Hardness	-	170
Impact resistance (Charpy)	kJ/m²	n.b
Friction coefficient	-	0,34
Glass transition	° C	-60

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2. MATERIALS AND METHODS

The polymer of this research is Polyoximethilene manufactured by RADICI® under the commercial name of HERAFORM R900 Copolymer. This material is used in different industrial application such as water drain valves, car intakes and oil pumps. Specimens were injection molded in Haitian Plastics Machinery® - MA 1200. The parameters of injection process can be seen in tab. 2

Table 2. Parameters of the injection process.

Parameter	Unit	Value
Injection pressure	MPa	236
Screw diameter	mm	36
Injection rate	g/s	112
Clamp tonnage	kN	1200
Melt temperature	°C	200-220
Mold temperature	°C	80-100

The specimens were stored in a chamber at a temperature of 23 °C and the relative humidity of 50%. The samples have been tested dry as molded.

The mechanical properties are influenced also by the injection parameters: speed and pressure of process and temperature of the injection matrix (Belmonte et al., 2017; Banaceur, 2008) and the strain rate, temperature of the test. The temperature dependency of thermoplastic implies that they are soft when heated and rigid when cooled. POM are known to be temperature subordinate with the increment of the temperature, a reduction in the stiffness, in the Young's modulus and failure stress is observed and an increase in the failure strain leading to higher ductility.

Also, the increase of temperature can increase the moisture absorption of the material (Chevali et al., 2010; Mouhmid et al., 2006). Associated with the loss of mechanical properties when temperature increases, thermoplastic composites soften when reach temperatures closer to the melting temperature, *Tm*, and potentially conducting to the ineffectiveness of structural applications. It is well known that organic materials exhibit viscoelastic transitions followed by reversionary and irreversible thermal degradation process when submitted to high temperature, especially at temperature close to *Tm*. The elastic modulus of a polymer will be significantly reduced closer to *Tm*, due to the fact that variations of temperature promote modifications in its molecular configuration.

In order to assess the effects of diesel and biodiesel on the POM polymer samples, compatibility tests were carried out. The experiment consisted of soaking the sample in Diesel during a period of 10000 hours at low (-10ºC), room, (23ºC) and high temperature (60°C), simulating an extreme case of fuel exposure in an automotive system. Figure 2 present the mentioned specimens:

Figure 2. Specimens under the effect of diesel. (A) Specimens at -10 °C (B) Specimens at room temperature (C) Specimens at 60 °C.

Polymer tensile bars, with dumbbell shape, according to ASTM D638, were employed to run the tests. Samples of each poly were placed inside special containers designed to resist fuel compatibility tests. The containers were filled with diesel, sealed and introduced into a cold and hot chamber. Sampling was carried out at 1000, 2000, 3000, 5000 and 10000 hours. Mechanical properties of the specimens were tested using a Shimadzu AG-X universal testing machine with a of 100 kN capacity load cell and electro-mechanical sensors to control the transverse displacement and with a cross-head rate of 5 mm per minute. Figure 3 presents the specimen under test.

Figure 3. Specimens under testing.

3. RESULTS AND DISCUSSION

Figures 4, 5 and 6 shows the stress vs. strain curves of POM polymer immersed in Diesel at different temperatures: -10ºC, room temperature (23ºC) and 60ºC, for different periods of time (0, 1000, 2000, 3000, 5000 and 10000h).

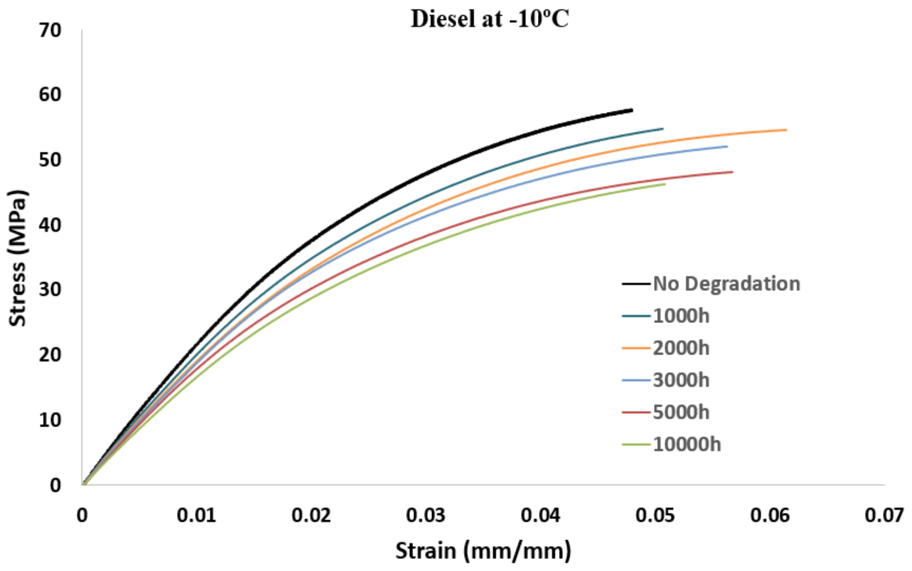

Figure 4. Results at -10 °C.

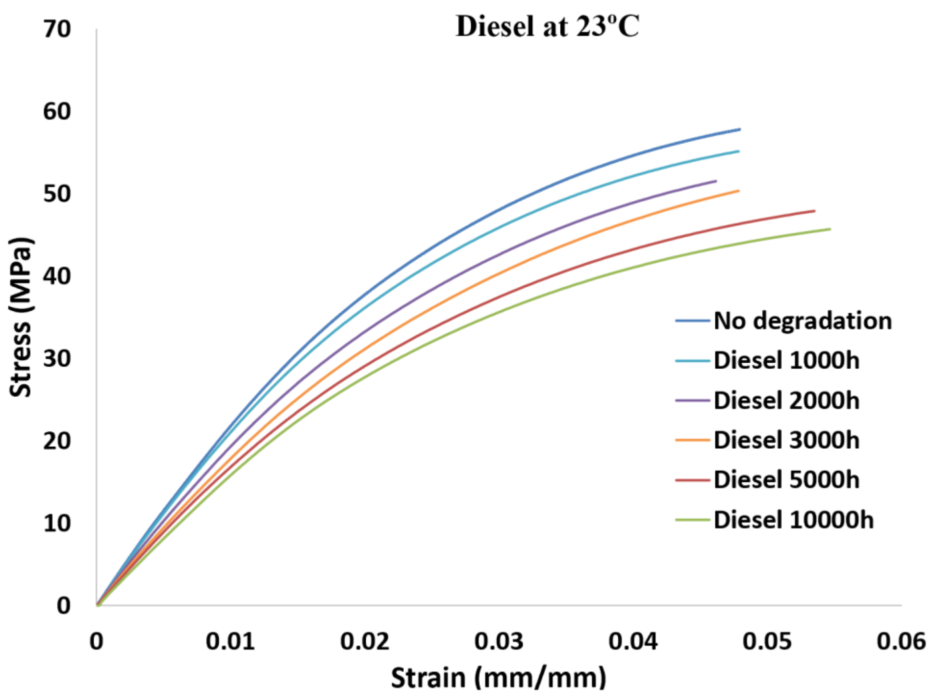

Figure 5. Results at 23 °C.

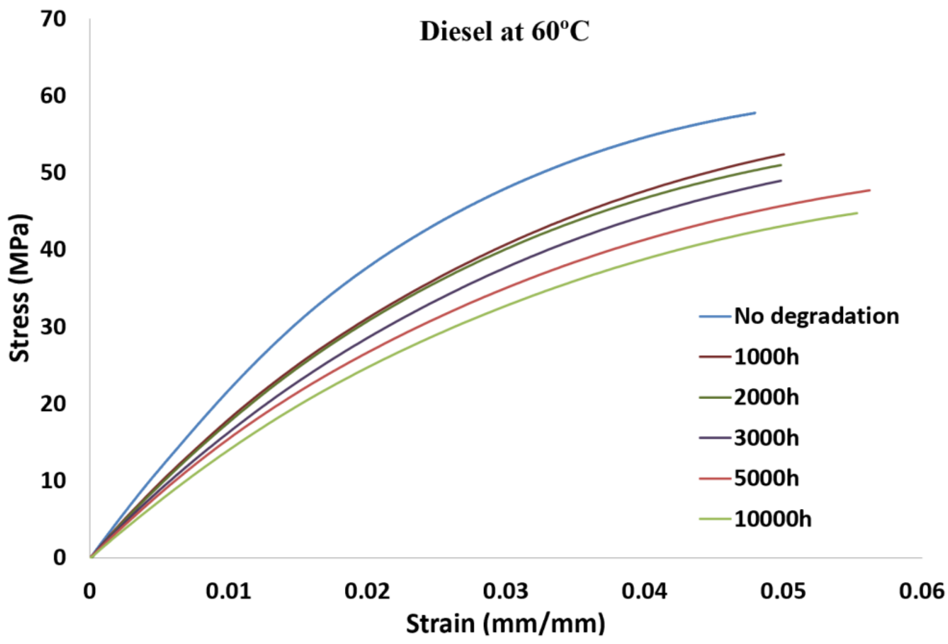

Figure 6. Results at 50 °C.

From figures 4, 5 and 6 can be seen a significant decrease in the mechanical properties of POM when immersed in diesel at different temperatures. At each exposure temperature the stiffness and tensile strength were affected as exposure time increase. It is observed a decrease in the modulus of elasticity as well as failure strength. This is associated with the low chemical resistance of POM (Fayolle et al. 2008, 2009). Despite the loss in the mechanical properties observed, the strain at failure remains unaltered of all tested conditions.

The immersion in diesel at different temperatures led, after 10000h a degradation of 20% in the tensile strength, presenting the higher degradation for 60ºC (22.8%). Considering the modulus of elasticity, a diminish of 24.2% is calculated for POM immersed in diesel at -10ºC, 31.9% for POM immersed in diesel at 23ºC and higher decrease is reported for POM immersed in diesel at 60ºC, 36.8% lower. Overall, diesel severely degrades POM compromising its long-term used when immersed in such solutions.

The mechanical degradation observed in POM is mainly produced by oxidation. This oxidation affects the amorphous parts of the material, leading chain scissions and depolymerization processes. This entanglement amorphous network is responsible for the ductile behavior of the, keeping connected the crystalline parts. The shortening of the chains reduces the ductile behavior, while the monomers produced during the depolymerization can be included in the crystalline part. This process is called “chemi-crystallization” and consists on the increment of the crystalline proportion in the material. The consequence of this increment is the considerable increment of the embrittlement. This has also been noticed through the visual analysis of the fracture surface and structure of the different blends.

4. CONCLUSIONS

The aim of this work was to evaluate the long-term mechanical degradation of POM in contact with diesel at different temperatures. POM is highly used in the automotive industry due to its low weight and high resistance to chemical especially in fuel pumps which are inserted straight into the tank making POM directly in contact with the fuel.

Although highly resistant to chemicals, the direct contact with diesel at different temperatures reduces POM long-term mechanical properties by one third. Such factor should be taken into consideration when designing long term structures that have contact with diesel, considering that it can decrease significantly its life. It was expected a degradation in the mechanical properties to POM when immersed at 60ºC since exposure to elevated temperatures considerably reduces polymers performance, and it was confirmed by the experiments. A similar behaviour was observed is the specimens immersed at -10, where a clear degradation was seen.

The reduction in the mechanical properties observed when POM is immersed in diesel at room temperature and at -10ºC reinforces the premises that the main degradation factor most likely due to the oxidation process.

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7. RESPONSIBILITY NOTICE

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