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STUDY OF THE EFFECTS OF FAM B (TEST FUEL) ON THE MECHANICAL PROPERTIES OF AN AUTOMOTIVE POLYMER FROM THE POLYAMIDE FAMILY (PA)

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ABSTRACT

Since last decades the use of polymers in the automotive industry is rising. They can be found in several systems of a carwith the requirements of the materials employed in agreement with the neededperformance. For polymers in direct contact with fuel, special characteristics are needed, such as the retention of mechanical properties and dimensions. Thus, compatibility tests between polymers and fuels are essential to guarantee a good performace during functioning. FAM B is a common test fuel used to validate the polymers behavior in conditions similar to the ones experienced by the material in application environment. In this paper, the behavior of a 35% glass reinforced polymer from the Polyamide family (PPA) exposed to FAM B at 60°C during 336 hours was studied. Dimensions and mechanical properties were evaluated periodically to observe the evolution of the polymer performace under these conditions. Infrarred spectroscopy (FTIR), Differential Scanning Calorimety (DSC) and Thermogravimetric Analysis (TGA) techniques were also employed to complement the study.

KEYWORDS: Polyamide, PPA, compatibility, FAM B, fuel, Mechanical properties.

INTRODUCTION

Automotive industry is in constant evolution. Lighter, cleaner and less expensive automobiles have to be designed to fit with the new global demands: lower emissions to reduce greenhouse effect, lower cost to be competitive in the actual market, etc. A reduction of 10% car weight economizes fuel in 7% and for each kilogram of weight reduction the carbon dioxide emissions diminishes in 20 kg. [1]. These are the reasons why polymers are being used to substitute metallic parts [2].

In order to substitute metallic parts from any automotive component, the special characteristics that polymers must accomplish have to be determined carefully. These characteristics will depend on the application. For example, a component of the fuel handling system which is directly exposed to fuel and heat requires an engineering polymer resistant to chemicals and temperature. Also, it is important to consider that component dimensions should be maintained to avoid problems in the application: dimentional changes could lead to the component failure.

It is common to find several types of polymers in a fuel handling system depending on the application of the component. The most common polymers found in this system are: Polyoxymethylene or acetal (POM), Polyphenylene Sulfide (PPS) and Polyphthalamide (PPA), among others.

For cases where chemical and temperature resistance are critical, PPA polymers are selected to conform the component.With the aim to determine if these polymers are adequate to be used in the fuel handling system Compatibility Tests are carried out.

Compatibility tests are an important tool that allows to observe the effect of a certain fluid over a determined material in controlled conditions.

Polymers can be tested with the fluids they are in direct contact with or by using more aggressive substances which allow to evaluate the worst case scenario.

This is the case of FAM B. FAM B is a test fuel commonly employed in Europe to test polymers that will be in contact with fuel. It contains a mixture of toluene, methanol, isoctane, etc. [3, 4] that can be very aggressive with polymers.

For this paper a Polymer from the PPA family was selected to be tested with FAM B with the purpose of understanding the effect of fuel exposure on the mechanical properties of ththe PPA polymer.

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MATERIALS AND METHODS

Materials

A Polyphthalamide (PPA) polymer with 35% glass fiber employed in fuel handling components was selected for this study. PPA materials generally are more robust than other polymer families such as acetals (POM), because they contain aromatic rings (Figure 1) which provide heat stability and good mechanical properties [5]. PPA materials are considered as a high performace polyamides. Tensile bars of this material with dumb-bell shape, according to ASTM D638 [6] and ISO 527 [7, 8] were employed to perform the compatibility test.

The selected fuel was FAM B, a non commercial fuel test, employed generally in Europe, and appropriate only for testing purposes [3]. Methanolic FAM testing fluid is used for automotive industry to evaluate the performance of polymers regarding dimensions, mechanical properties, hardness, etc. There are FAM A, FAM B and FAM C. For this work, FAM B was prepared according to DIN 51604 [4]: 84.5% FAM A, 15% methanol and 0.5% water, where FAM A is 50% toluene, 30% isooctane, 15% diisobutylene and 5% methanol.

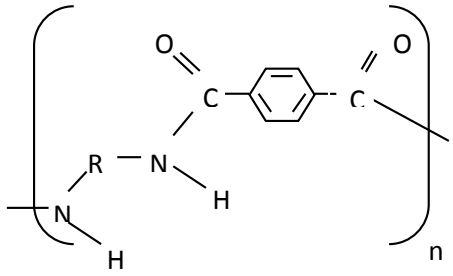

Figure 1. Polyphthalamide basic unit

Methods

Compatibility test consisted on the soaking of the tensile bars in FAM B. Tensile bars were located inside a stainless steel container specially designed for compatibility tests. The container was filled with fuel FAM B until the polymer samples were completely covered by it and then it was sealed. Once closed, the container was placed inside a chamber at a constant temperature of 60°C during 336 hours. Sampling was programmed at 48, 168 and 336 hours to observe the changes in the polymer characteristics. Five specimens were taken at each sampling. Mechanical properties were tested using an Instron 5581 machine with a clip-on extensometer according to ISO 527 [7, 8]. The specimens were tested along its longitudinal axis at a constant speed (5 mm/min) until the specimen fracture was achieved. As a result the mechanical properties measured were: Tensile strain at yield, Tensile stress at yield, Tensile strain at break, Tensile Stress at Break, Young's Modulus and energy to break.

Fourier Transform Infrared Spectroscopy (FTIR) was employed to compare the polymer structure before and after the soaking. Tests were run using a FTIR Nicolet iS10, Smart iTR from Thermo Scientific, with a 4 cm^{-1} resolution in the wavenumber range of 4000 - 500 cm^{-1}.

Differencial Scanning Calorimetry was used to determine the melting point of the polymer before and after the fuel immersion. Thermal analyses were run using a Differential Scanning Calorimeter 8500 with hyperDSC, from Perkin Elmer with a temperature ramp of 10°C/min.

Thermogravimetric analysis were performed with a Thermogravimetric Analyzer Pyris 1 from Perkin Elmer, with a temperature ramp of 10°C/min.

RESULTS AND DISCUSSION

Dimensions and weight change

Dimensional stability is an important characteristic that polymers used in automotive industry must have. A dimensional change in some key components can cause the failure of the system. Thus it is essential to verify that, even when the polymers are exposed to certain fluid, they retain their dimensions.

In this case of study, PPA samples exposed to FAM B at high temperature showed a volume change of almost 10%, reaching 5% during the first 48 hours (Figure 2).

Regarding weight change, it increased almost 5% during the first 48 hours, having a maximum increase of 6% at the end of the experiment compared with the original weight.

In a real application, volume changes should be evaluated carefully to assess the impact in the component functionality.

Mechanical Properties

Retention of mechanical properties of polymers is essential to guarantee a good performance in the application. In general, it is desired to minimize the variation of these properties.

A summary of mechanical properties variation is shown in Table 1.

Tensile stress at yield represents the stress at wich polymer starts to deform plastically, in other words, when it starts suffering non-reversible changes.Figure 3 shows the variation on Tensile stress at yield of PPA samples after exposure to FAM B. It can be observed that this property diminishes almost 30% during the first 48 hours, reaching a maximum decrease of 50% at the end of the test (Table 1). This

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means the PPA samples exposed to FAM B after 48 h will permanently deform easier than before the immersion. They require lower stresses to suffer non-reversible changes compared with non-exposed samples. This can be explained due to solvation: the fuel is polar and cause attraction to some molecules of the polymer, reducing intermolecular forces between the polymeric chains.

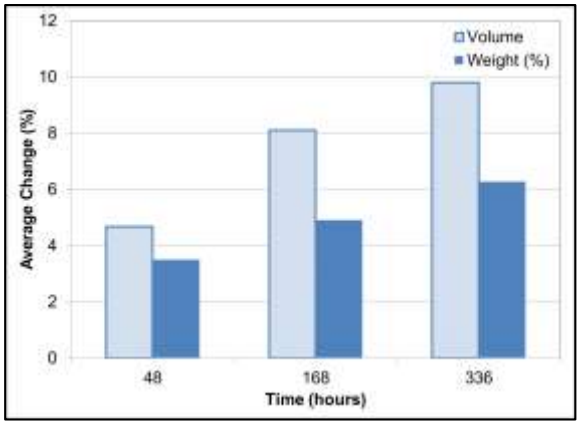

Figure 2. Dimensional and weight change

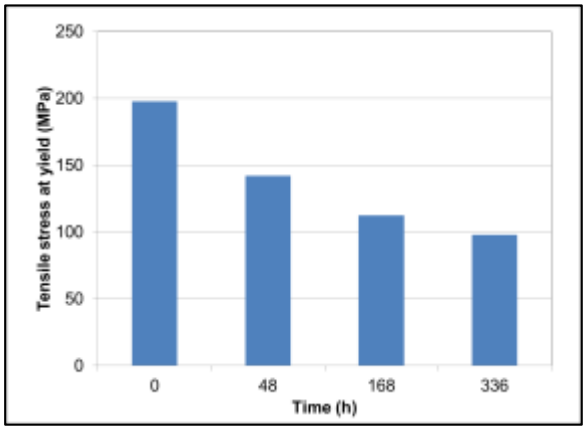

Figure 3. Tensile stress at yield (MPa)

Tensile stress at break measures the stress required to break the sample. A similar behavior to the observed with tensile stress at yield was seen with tensile stress at break for PPA samples exposed to FAM B (Figure 4). Samples exposed to FAM B for a period of 336 hours broke with 50% less load than the unexposed samples.Again, the main changes occurred during the first 48 hours of fuel exposure.

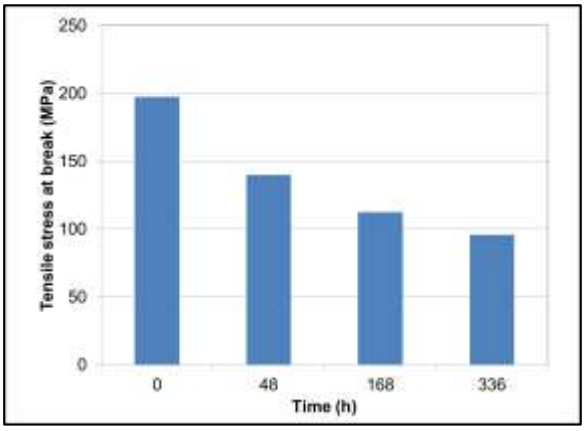

Figure 4. Tensile stress at break (MPa)

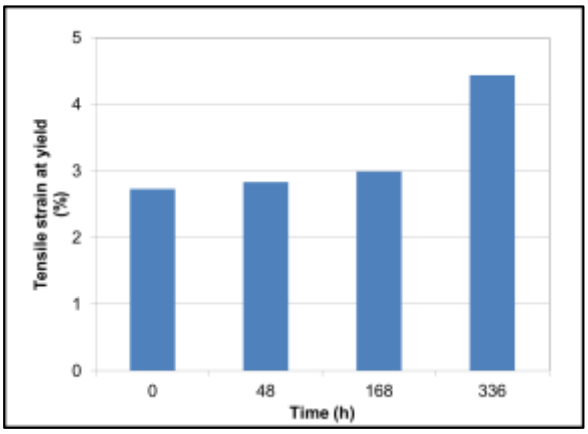

Figure 5. Tensile strain at yield (%)

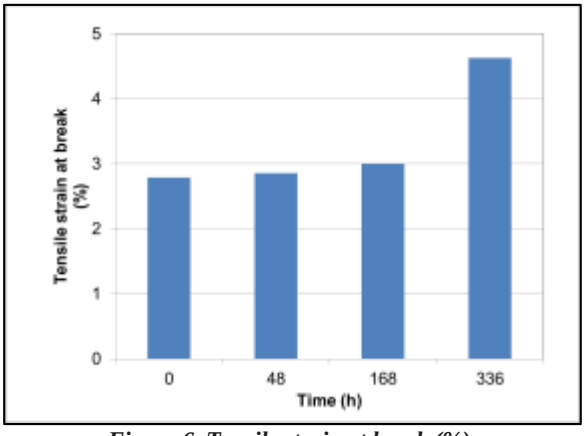

Figure 6. Tensile strain at break (%)

Tensile strain at yield accounts for deformation at the point where sample starts to be deformed plastically. It measures the increase in length compared to the original length. In Figure 5 the variation of this property against fuel exposure time can be seen. It can be noticed, that tensile strain at yield increases with fuel exposure from 2.7% to 4.4%. This is a

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strain approximately 60% larger than the original strain.

In a similar way, tensile strain at break measures the deformation at the point when sample is broken. Figure 6 shows that PPA samples exposed to FAM B got an increase on this property, changing from 2.8% to 4.6%. This represents an increase of 66% in the original strain.

According to ISO 527 [7], Young's Modulus represents the slope of stress/strain within the proportionality zone. It is a key property that shows the relationship between the applied stress and the deformation caused in the specimen. A decrease in the slope means that the sample requires a lower stress to reach a certain deformation , in other words, the sample is more prone to deformation.

As it can be noticed in Figure 7, exposure to FAM B caused that PPA samples were more prone to deformation, due to a Youngs' Modules decreasement of 38% (Table 1).

Concerning the energy required to break the sample, it was reduced more than 50% after 336 hours of fuel exposure. This value diminished 30% during the first 48 hours.

All these changes can be explained because of the fuel absorption by the polymer. As mentioned before, the polar nature of the fuel causes the attraction of some molecules in the polymer, causing its solvation or plastification. This behavior, reduces the intermolecular forces in the polymer chain, producing swelling, an increase in elongation and impact strength, among others. This is in aggrement with the reported by Scheirs [9].

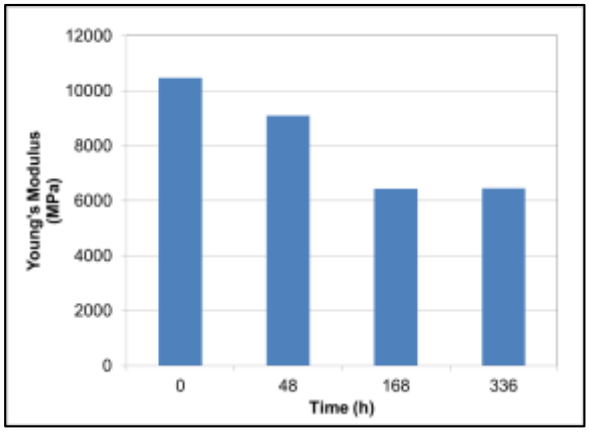

Figure 7. Young's Modulus (MPa)

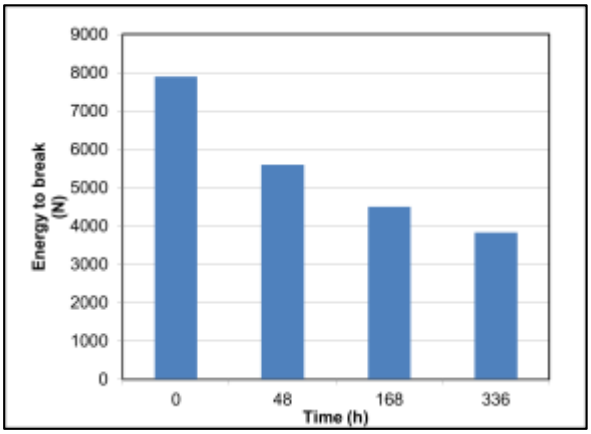

Figure 8. Energy to break (N)

Fourier Transform Infrared Spectroscopy

Fourier transform Infrared spectroscopy (FTIR) was employed to observe the occurrence of structural changes during soaking.

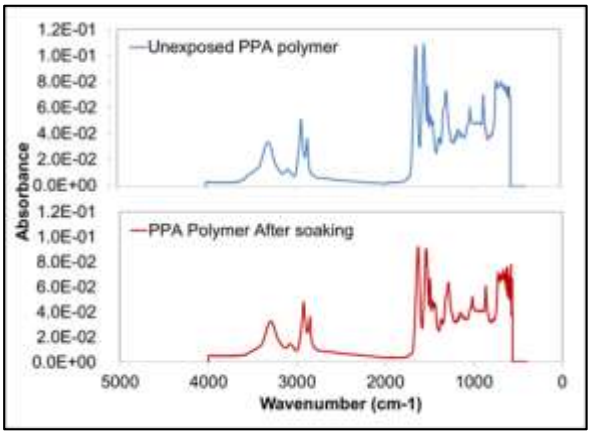

Figure 9. FTIR spectra of unexposed and soaked sample

As can be seen from figure 9, spectra of both samples, the unexposed one and the one soaked during 336h, exhibit a similar behavior. Two broad absorption bands are present, one from 1690 to 560 cm^{-1}, and another one from 3660 to 2810 cm^{-1}. These bands are characteristic of the C-H stretching of the aliphatic hydrocarbons, which absorb from 1460 to 1380 cm^{-1}, and the stretching of primary and secondary aliphatic amides NH- and NH_2- ,that absorb from 1570 to 1515 cm^{-1} and from 3320 and 3070 cm^{-1} [10]. There are no difference between both spectra.

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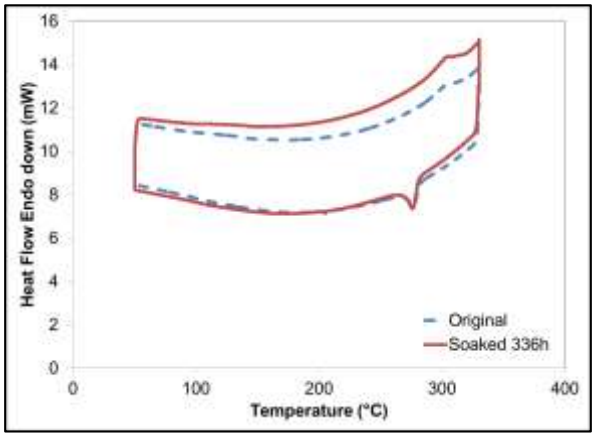

Figure 10. DSC thermograms of unexposed and soaked sample

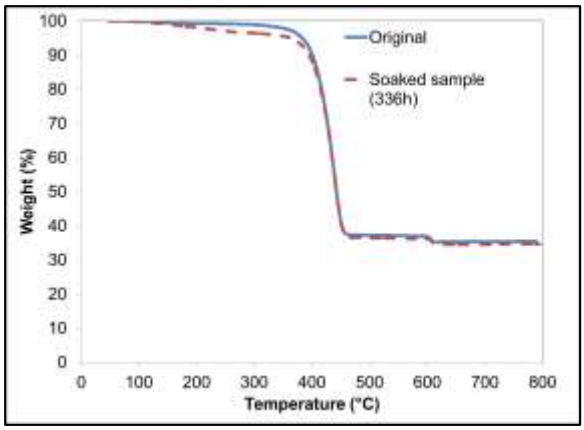

Figure 11. TGA thermogram of unexposed and soaked sample

Differential Scanning Calorimetry

Figure 10 shows the DSC thermograms corresponding to the original and the soaked sample (336h), tested from Room Temperature to 300 at 10 °C/min measuring the changes during heating and cooling. Exothermic and endothermic curves are shown for both samples. As it can be seen, the melting point of both sample types (unexposed and soaked) is the same (277°C), as well as the recristalyzation point.

Thermogravimetric Analysis

Regarding Thermogravimetric analysis, thermograms are shown in Figure 11. It can be observed thatthe differences between exposed and unexposed samples are not significant (less than 3% in the range of 190 to 400°C), and may be due to experimental variations.

Table 1. Mechanical properties

	Initial	Final	Change %
Tensile stress at Yield (Mpa)	197.6	97.9	-50.5
Tensile stress at Break (MPa)	197.3	95.7	-51.5
Tensile strain at Yield (%)	2.7	4.4	62.5
Tensile strain at Break (%)	2.8	4.6	66.1
Young's Modulus (MPa)	10474.6	6447.2	-38.4
Energy to break (N)	7893.8	3828.2	-51.5

CONCLUSION

A compatibility test between a testing fuel (FAM B) and a high resistant engineering polymer (from PPA family) commonly used in automotive industry was carried out.

Mechanical properties of the selected polymer were dramatically affected by the fuel soaking at high temperature. With 336 h of exposure, the polymer properties changed more than 60%, which is not recommended for automotive applications, were property retention is essential:

- Tensile stress at yield was reduced in 50%, indicating that samples required less stress to be permanently deformed.
- Tensile stress at break diminished 51%, thus the samples brakes easier.
- Tensile strain at yield increased 62.5%, indicating a bigger deformation when a stress is applied.
- Tensile streain at break augmented 66%, which means that deformation before breakage augment.
- Young's Modulus was reduced 38%, indicating that samples are more prone to deformation with a lower stress, compared with the non-exposed material.
- Energy to break was reduced 51%.

These changes indicate that the polar nature of fuel absorbed by the polymer probably interacted with the polymer molecules plasticizing or solvating the

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material and, consequently, affecting its mechanical properties.
Thus, the use of this material for automotive applications should be carefully evaluated, according to the function performed by the element where this material is present.
No significant differences were observed by thermal techniques (DSC, TGA analysis) nor by infrared spectroscopy (FTIR).

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